SYNTHETIC CROSSLINKING OF POLY (VINYL ALCOHOL) FOR USE IN A SYNTHETIC ARTICULAR CARTILAGE

by

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January, 1972

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Chairman
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ABSTRACT

SYNTHETIC CROSSLINKING OF POLY (VINYL ALCOHOL)
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Submitted to the Department of Chemical Engineering on January 21, 1972, in partial fulfillment of the requirements for the degrees of Bachelor and Master of Science

As a continuation of initial efforts to develop an articular cartilage replacement, this work was aimed at improving, via selected crosslinking techniques, the toughness and durability of the basic component, crosslinked poly (vinyl alcohol), by creating a highly crosslinked, highly concentrated product. Poly (vinyl alcohol)--a tough, flexible, hydrophilic, shock-absorbing material capable of ultrafiltration for lubrication purposes--was selected for its similarity of physical characteristics to articular cartilage.

After a review of available crosslinking methods, two promising free radical initiated methods were selected: 1) a chemically initiated oxidation-reduction system and 2) a 3 M.E.V. β^- -irradiation induced method. Five difunctional crosslinking monomers--allyl acrylate, allyl methacrylate, diallylamine, N'-N'-methylene bis acrylamide, and tetraethylene glycol dimethacrylate--were selected to act as the only crosslinking means in method one and to enhance crosslinking of poly (vinyl alcohol) alone--i.e., exclusive of the crosslinking monomer--already present in method one.

N'-N'-methylene bis acrylamide alone showed signs of crosslinking when added to poly (vinyl alcohol) in the redox system. The system as a whole lacked promise of providing the desired crosslinked highly concentrated product, for only low viscosity solutions--i.e., 5-10% poly (vinyl alcohol)--could effectively be reacted.

Irradiation of aqueous 20% poly (vinyl alcohol) containing N'-N'-methylene bis acrylamide showed enhanced crosslinking at total doses between 3 megarads and 15 megarads, but was especially pronounced at the lower doses. Furthermore, irradiation of samples of increasing concentration above 20% poly (vinyl alcohol) showed increased enhancement of the crosslinking.

The other crosslinking monomers used in the irradiation method either partially poisoned--allyl acrylate, allyl methacrylate--totally poisoned--diallylamine--or did not effect--tetra ethylene glycol dimethacrylate--the poly (vinyl alcohol) crosslinking already present.

Thesis Supervisor: Dr. E. W. Merrill
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January 21, 1972

Professor David B. Ralston
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dear Professor Ralston:

In accordance with the regulations of the Faculty, I herewith submit a thesis entitled "Synthetic Cross-linking of Poly (vinyl alcohol) for Use in a Synthetic Articular Cartilage," in partial fulfillment of the requirements for the degrees of Bachelor of Science and Master of Science in Chemical Engineering at the Massachusetts Institute of Technology.

Respectfully submitted,

TIMOTHY H. DE COOK

ACKNOWLEDGEMENTS

Special thanks go to Professor E. W. Merrill for his proposal of this thesis topic and continued confidence in the author's efforts.

The author is deeply indebted to James Bray for his assistance, comments, general enthusiasm, and overall guiding hand throughout this work.

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I. SUMMARY

A. Introduction

The work documented herein was a continuation of the pioneering efforts of Geist (32) to develop a material suitable for articular cartilage replacement. Using a previously developed base material of 5% crosslinked, aqueous poly (vinyl alcolol)--PVA--Geist worked mainly on the surface chemistry aspects he felt necessary for the success of an articular cartilage prosthesis. This thesis was initiated to improve the crosslinked PVA backbone, via selected crosslinking techniques, by creating highly concentrated, highly crosslinked PVA.

1. Rationale

Articular cartilage is necessary for weight-bearing joints to function properly, as it lines the heads of bones in contact at these joints and provides 1) lubrication by a viscous polymer, hyaluronic acid, for smooth joint movement, and 2) transmission of applied pressures to surrounding tissues. While the exact mechanism of joint lubrication can presently only be postulated, the force transmission mechanism of cartilage is fairly well understood. Cartilage is essentially a hydrophilic, and hence, normally water swollen, network of tough collagen fibers. When stressed, these fibers extend to transmit

the force while absorbed water acts as a cushion.

To accomplish the two functions noted above the synthetic cartilage should be a highly crosslinked PVA material of high concentration to attain durability, flexibility, and a hydrophilic nature. A highly crosslinked network is necessary not only for durability but also to provide slow steady rates of fluid absorption and expulsion to help maintain a constant lubrication film when stressed.

2. Chemistry

A crosslinked material is a three-dimensional network. To crosslink a linear polymer--viz., PVA--a means of initiation is required--free radical initiation is widely used and was the method employed in this work. Once reactive free radicals are formed within a polymer chain--not on the ends, however--crosslinking can occur between the polymer and another polymer molecule either directly by the coupling of two radicals on separate molecules (fig. 1)

(fig. 1)

or indirectly through a crosslinking agent; in this case, the polymeric radical attacks a reactive double bond, known as a functional group--crosslinking agents have two or more

such groups. Both the newly formed radical and the remaining functional group on the crosslinking agent (fig. 2) can react with another polymer molecule to finalize the crosslink.

(fig. 2)

B. Procedure

Two means of radical initiation were selected: 1) a redox system involving a chemical initiator, and 2) an irradiation method involving high energy--3 M.E.V.--electrons. Of the two, the second was by far the cleaner--i.e., no contaminating chemicals were necessary--simpler, easier, and more efficient.

Although the redox system required a crosslinking agent, the radiation system did not, as PVA irradiated under proper conditions (49) would readily form its own crosslink bridges. Bray (5), however, found a complicating factor with the irradiation method: irradiating increasing concentrations of PVA under similar conditions led to decreasing degrees of crosslinking. Therefore, crosslinking agents were utilized in this work in hopes of eventually enhancing the irradiation-induced crosslinking of highly concentrated PVA aqueous solutions.

C. Discussion of Results and Conclusions

With one exception the redox system showed negative results of crosslinking PVA solutions--the use of the crosslinking agent N'-N'-methylene bis acrylamide showed signs of crosslinking PVA. The two major drawbacks of this system were that 1) only low viscosity and hence low concentration PVA solutions-- 5-10% PVA --could be mixed effectively and 2) the final product was an amorphous mass very difficult to analyze.

The results from the irradiation method were more extensive. As crosslinking of PVA via its own bridging action occurred during irradiation, all results utilizing crosslinking agents were compared to a pure PVA sample irradiated under similar conditions to check for enhancement of diminishing of the crosslinking.

Of five crosslinking agents added to 20% PVA aqueous solutions, only one-- N'-N'-methylene bis acrylamide-- seemed to enhance PVA crosslinking at total doses between 3 and 15 megarads (see Chart II). The other four crosslinking monomers--allyl acrylate, allyl methacrylate, diallylamine, and tetra ethylene glycol dimethacrylate-- either partially or totally poisoned crosslinking--the case of the first three listed monomers--or had no apparent effect when irradiated with PVA over the same dose ranges.

Crosslinking enhancement by the N'-N'-methylene bis acrylamide--as well as the diminishing effect of a poisoning crosslinking monomer--was greatest at low doses (see Chart II)--i.e., three megarads--where the crosslinking agent could compete with PVA's own crosslinking action. At higher doses, all added crosslinking agents which did not totally poison crosslinking had little effect--all crosslinking was essentially by PVA alone.

Finally, and most important, N'-N'-methylene bis acrylamide showed increasing crosslinking enhancement with increasing PVA concentrations above 20% PVA aqueous solutions. This indicates that addition of the proper crosslinking agent to PVA prior to irradiation may yield the desired highly crosslinked, high concentration PVA.

II. INTRODUCTION

A. General

In 1971 Geist (32) published the results of his efforts to develop a synthetic articular cartilage for joint replacement. His work centered on fixing charged groups onto water-swollen, crosslinked poly (vinyl alcohol)--PVA--networks--approximately 5% PVA by weight--known as hydrogels, developed by Merrill and Wong (43,57), in order to create a surface active material which, theoretically would provide sufficient joint lubrication to act as a cartilage prosthesis. Geist's work was the pioneering work of what is viewed as a seven year project for the MIT Chemical Engineering Department's biomedical engineering group. The author's work in this group was to investigate methods of crosslinking PVA to create a tough, resiliant, hydrophilic network of much higher PVA weight per cent than the hydrogels to serve as the body of the synthetic cartilage--we were convinced that the hydrogels, being 95% water, could not long withstand the constant stress--at times in excess of 2000 lbs/sq in. (40)--applied to articular cartilage.

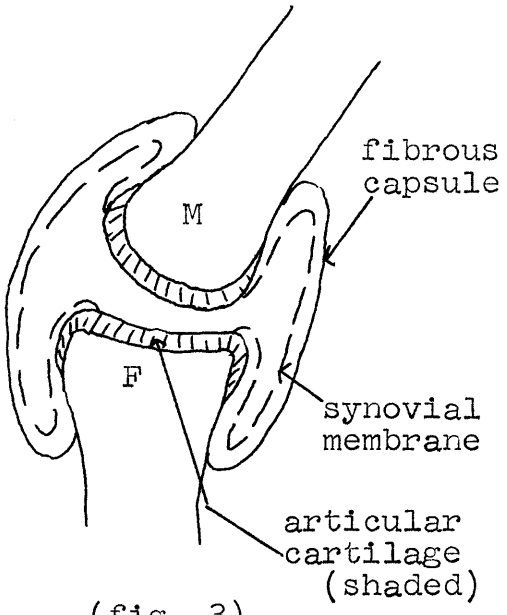
B. Medical Criteria

The structure and functions of joints in the body, and in particular articular cartilage, has received a

a great deal of attention in the last few decades (22, 24,28, 37, 38, 40). Any prosthesis must duplicate the absorbing and lubricating functions of this cartilage.

Of interest to this thesis are the synovial, weight-bearing joints of the body. Articular cartilage, the smooth gristle lining of the jointed surfaces takes and transmits applied stresses to the surrounding capsule and reduces friction in the process. Destruction of the articular cartilage from disease and injury and subsequent joint wear can be extremely crippling. A successful replacement for this diseased cartilage is the ultimate goal of this group project.

Essentially all synovial joints of the body are weight-bearing with a common structure modified by the intra-articular cartilage--articular cartilage not capping the connecting interfaces within the joint. A typical synovial joint (fig. 3) consists of at least one pair--male (M) and female (F)--of mating surfaces enclosed completely by a fibrous capsule and bathed in synovial fluid, which provides lubrication and nutrition



(fig. 3)
(37)

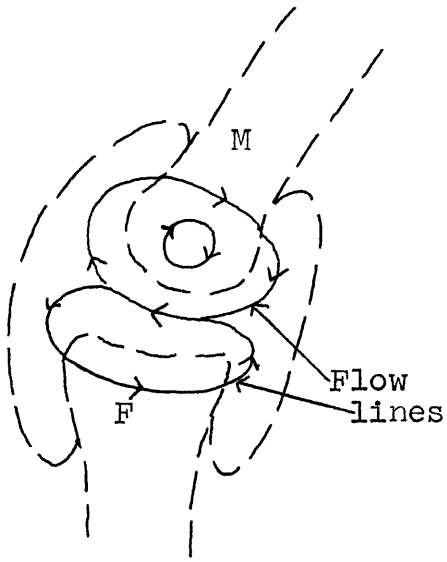
to the joint. Muscular forces, gravitational forces, or a combination of both keep the cupped surfaces of the joint in constant contact.

Mac Conaill (39) found that the surface of articular cartilage is a thin, non-collagenous, true cartilage layer, below which collagen fibers intermesh parallel to the surface. Further study has shown this fibrous mesh to be a three-dimensional network of collagen fibers, composing 47 to 66% of the total dry weight, complexed with a mucopolysaccharide, chondroitin sulfate, composing 16 to 25 % of the total dry weight. The chondroitin sulfate not only crosslinks the collagen, creating an elastic network with high tensile strength, but also binds to water and other cations, suggesting a role in the hydrophilic nature of cartilage (46). The collagenous, spongy network between and around bones at the joints provides elasticity yielding deformation under an applied stress. As the network spreads under compression, the crosslinks eventually resist further deformation and bring the network back to its original relaxed state when the stress is released.

Mc Cutchen's permeability data (42) indicates that the matrix form of cartilage has pores approximately 60 Å in diameter. Further work by Linn and Sokoloff (36) has revealed that fully saturated cartilage is 70 to 80%

liquid with a composition similar to synovial fluid only lacking the inorganic sulfates and having a low viscosity--i.e., a fluid of low molecular weight components. These characteristics plus the fact that high pressures are applied to articular cartilage seem to imply the presence of an ultrafiltration process whereby only low molecular weight compounds freely pass through the cartilage.

The synovial membrane (fig. 3), completely surrounding the joint, contains blood vessels and nerves and is the boundary for the synovial fluid. This special fluid, an apparent dialysate of blood plasma with the addition of hyaluronic acid, a non-sulfated mucopolysaccharide, adheres to the articular surfaces and is dragged along by a moving joint. As a joint is a closed container, the synovial fluids also flows, probably by some streamlined motion (fig. 4), to the trailing edge at the joint of a rotating bone, thus constantly bathing the articular cartilage. The hyaluronic acid, molecular weight of about a million, which provides the bulk of the synovial fluid's viscous



(fig. 4)
(37)

nature, is a straight chain polymer with a large number of potentially charged carboxyl groups and, in vivo, forms a complex with protein--this complex is believed to be at the base of joint lubrication. The increased destruction with age of hyaluronic acid, and therefore this complex, by the enzyme hyaluronidase with resulting loss of joint lubrication and roughening of surfaces, is believed to be the cause of stiff joints in elderly people.

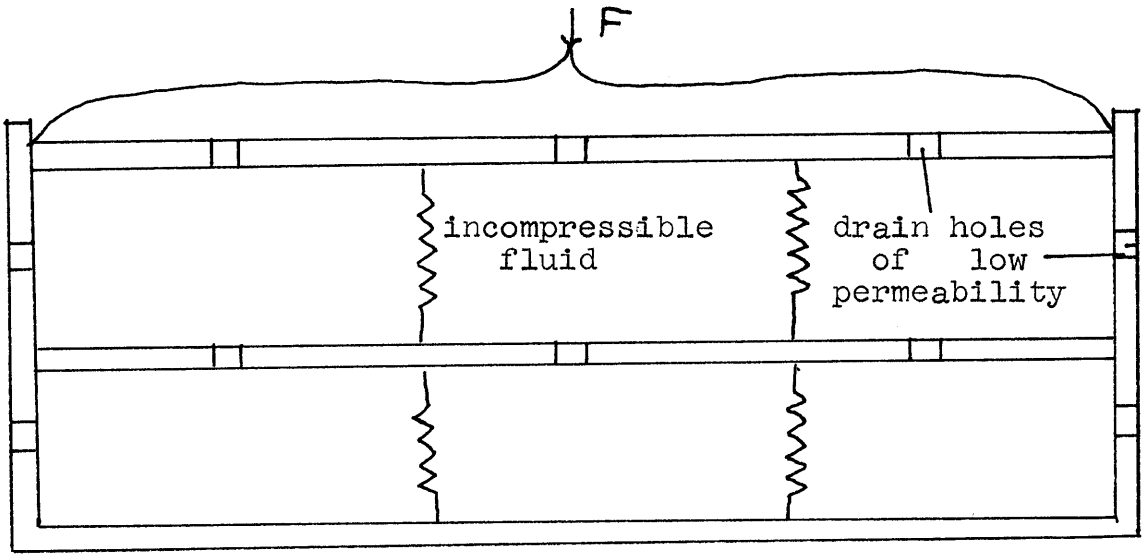
Many interesting theories to explain joint lubrication have been proposed and expanded upon in the last forty years (21, 23, 41, 56)--a good review of the more accepted theories is given by Geist (32). The mechanism of joint lubrication designed into the proposed prosthesis reflects some of the features of these theories but by the same token should be a viable means of lubrication no matter what the mechanism of natural lubrication proves to be.

C. Proposed Prosthesis

The basis tenants for the successful function of the proposed prosthesis are three fold: 1) forced absorption/ expulsion of synovial fluid by the synthetic cartilage; 2) a combined action of weeping bearing lubrication and osmotically-enhanced boundary lubrication discussed below; and 3) acceptance of the material by the

body upon implantation.

The emphasis of this work is on the first of these processes. A highly crosslinked, high concentration PVA material is planned to attain the required shock-absorbing properties of cartilage. The hydrophilic PVA will readily absorb the water-based, incompressible, synovial fluid excluding hyaluronic acid because of its size; the minute pores in the prosthesis, resulting from extensive

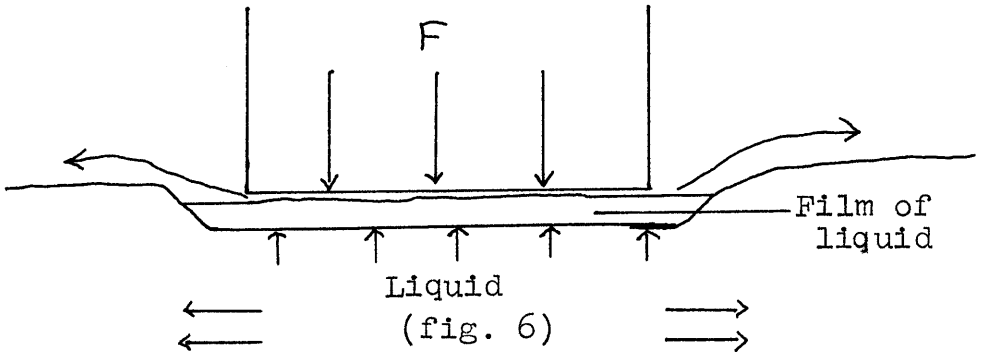


(fig. 5)

crosslinking (fig. 5)--(14)--will then allow only steady flow of the synovial fluid to neighboring cartilage and to the surface when local compression is applied by the contacting bones.

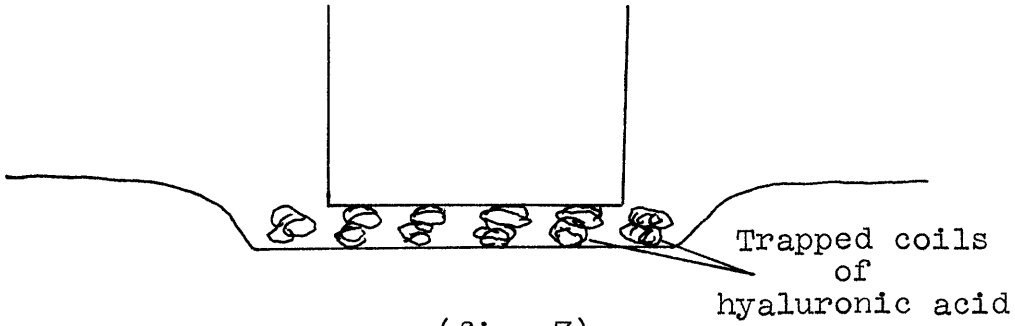
Lubrication in the joint at the point of compression will be enhanced as the incompressible synovial

fluid exuded to the surface will keep the opposing surfaces separated (fig. 6)--(14)--this is known as "weeping



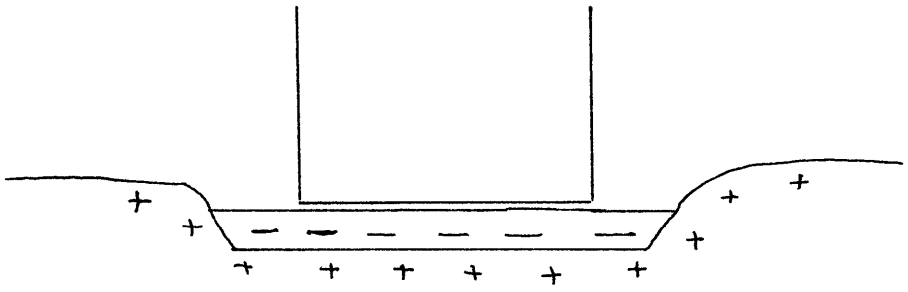
(fig. 6)

lubrication." Continued compression of the cartilage may completely "wring out" all absorbed fluids; in this case, the viscous, partially negatively-charged hyaluronic acid in synovial fluid will be unable to escape the contacted area due to its size and resulting low mobility, the effect being a viscous gel layer on the cartilage surface (fig. 7)--(14)--this is known as osmotically-



(fig. 7)

enhanced boundary lubrication. Brays' efforts (11) to graft cationic groups onto the surface of the synthetic cartilage to bond to hyaluronic acid are directed at preventing the erosion of the gel layer from shearing joint motion (fig. 8)--(14).



(fig. 8)

Bauers' initial efforts (5) on the third requirement show promise of eventual production of a non-thrombogenic PVA gel.

D. Crosslinking Methods

1. Terminology

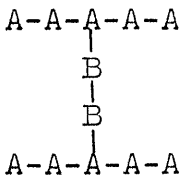
A linear polymeric molecule--viz., PVA--can be complexed in a number of ways when reacted with another molecule: 1) a block copolymer results when a second polymer bonds to the end of the original polymer molecule (fig. 9);

A-A + B-B ⟶ A-A-B-B (fig. 9)

2) a grafted polymer and copolymer are produced when unlike molecules and polymers, respectively, are attached to the internal portion of the initial linear chain (fig.10)

(fig. 10)

--a polymer grafted onto itself is termed a branch polymer; and 3) a single molecule which grafts to two or more of the initial polymer chains forms a crosslinked polymer (fig. 11).



(fig. 11)

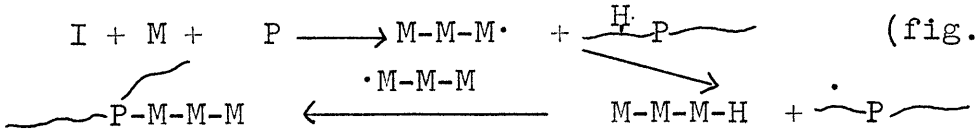
2. Criteria to Evaluate Crosslinking Methods

The following criteria are useful in evaluating available crosslinking methods used for eventual implantation purposes: 1) the equipment and procedures required should be as simple as possible to keep the chance of errors at a minimum; 2) the system should be free of toxic components, for extraction techniques are not always thorough enough--trace amounts of these components could initiate tissue rejection of the final implantable prosthesis; 3) the system should yield low concentrations, if any, of non-crosslinked homopolymer which contaminate

and weaken the product; 4) for reproducibility the system should possess a means of controlling the extent of grafting and the length of intermolecular chains; and 5) the final product should be in a readily analyzable form.

3. Chemical Routes

Several authors (3, 9, 29, 33, 55) discuss the various methods of producing crosslinked, or multiple grafted, polymers. A very common method is by radical attack on macromolecules in which a chemical initiator (I) begins the growth of monomer (M) chains which eventually abstract an active atom, such as hydrogen, from the polymer chain and graft at that point (fig. 12).



(fig. 12)

The presence of a toxic initiator plus non-crosslinked homopolymer in the final product is sufficient reason to reject this method.

A second general method of crosslinking is by direct formation of free radical initiators on the macromolecular chains. One technique, insertion along the main chain of hydroperoxide groups which, when converted to free radicals, graft monomer onto the macro-

molecule, is unacceptable due to its complexity and possible property alterations of the PVA networks. A second technique, investigated by Duke (25, 26), Mino and Kaizerman (3, 44, 45), and Singh (54), utilizes nitrate of sulfate ceric salts as effective redox systems with organic reducing agents such as alcohols (fig. 13), glycols, and thiols. The reaction produces cerous ions and free radicals exclusively on the polymer backbone--i.e., the addition of a vinyl monomer yields a graft with no homopolymerization of the monomer.

$$Ce^{4+} + RCH_2OH \rightleftharpoons [\text{Ceric-alcohol complex}] \rightarrow Ce^{3+} + H^{+} + (\dot{R}CHOH \text{ or } RCH_2O\cdot)$$

(fig. 13)

Detailed accounts of grafts of acrylamide and methyl methacrylate--reactive agents which have similar difunctional crosslinking forms--prompted further investigation of this crosslinking method.

4. Non-Chemical Routes

a. General

Three methods of non-chemically initiated free-radical cross-linking are widely used due to their simple initiation: 1) mechanical degradation--shear or stress applied to a polymer can cause free radicals at the broken ends, and, in the presence of the proper mono-

mer, yield a) block copolymers, or b) graft copolymers if chain transfer of the free radicals to the chain interior exists, 2) photochemical initiation, and 3) radiation initiation. The first method is unacceptable due to lack of grafting controls and the necessity of extensive chain transfer mechanisms for crosslinks to form. The selection of the third method over the second results from 1) the presence of two easily accessible radiation sources --a high energy β emitting source and a Cobalt 60 γ emitting source and 2) Geist's success (32) in grafting monofunctional monomers onto PVA via irradiation induced initiation.

b. Irradiation Routes

Five acceptable techniques of irradiation induced crosslinking exist (3): 1) direct irradiation of a pure polymer solution under an inert atmosphere; 2) direct irradiation of a polymer/crosslinking agent mixture under an inert atmosphere; 3) preirradiation of the polymer in air and then contacting it with monomer under an inert atmosphere; 4) preirradiation of the polymer under an inert atmosphere forming trapped radicals and then heating the polymer with monomer, also under an inert atmosphere; and 5) irradiation of polymer/crosslinking monomer emulsions in air.

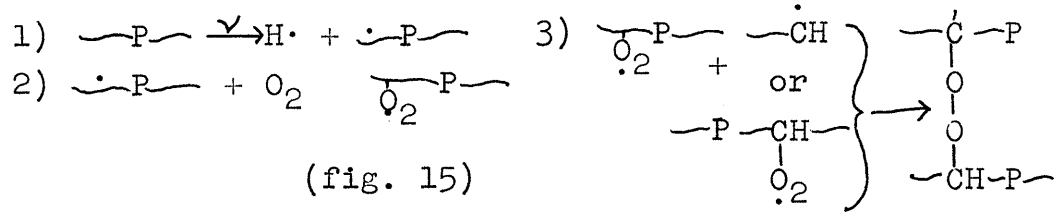
An irradiated polymer, whether pure or mixed with a crosslinking agent, can always crosslink itself by radical coupling of different chains (fig. 1, page 14). Thus the latter four methods of crosslinking are special cases of the first.

The second direct irradiation technique of crosslinking is the most efficient of the latter four, as the presence of the crosslinking monomer during irradiation allows immediate utilization of polymer radicals in bridge formation. Many polymer radicals in parallel pre-irradiation techniques are lost to hydrogen (H·), hydroxyl (·OH), and other radicals present during the interval between irradiation and monomer addition. Methods of reducing the undesirable homopolymer--monomer which polymerizes but does not crosslink--during direct irradiation include 1) irradiation in bursts allowing the crosslinking monomer to diffuse freely between intervals (16; 20), and 2) lowering the temperature during irradiation to a point where this monomer can not polymerize (58).

Several phenomena associated with the method of crosslinking by direct irradiation can greatly affect results (14) : 1) diffusion of the crosslinking monomer into the growing polymer network must keep pace with the rate of radical propagation if the crosslinking is to remain proportional to the dose rate (16, 17); 2) Hoffman,

et al, (34) have observed a continuation of crosslinking in some systems after irradiation, probably due to occluded unterminated chains--such an occurrence could well affect the correlation of dose to per cent crosslink; 3) chain transfer rates to solvents, monomer, and initiator can affect crosslinking rates and chain lengths, and 4) an increase in temperature during irradiation could easily have multiple effects: a) an increase in the diffusion rate of the crosslinking monomer, b) an increase in both the transfer and termination rates, c) reduction of the "gel" or autocatalytic effect, and d) an increase in solubilities. Thus, when crosslinking via direct irradiation, the variable parameters must be chosen to simplify the system as much as possible.

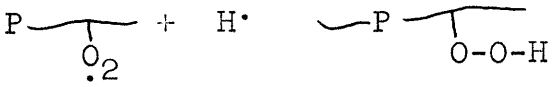
The method of polymer preirradiation in air involves insertion into the main chain of peroxide molecules which decompose to free radicals at approximately 150° C and initiate crosslinking only if sufficient monomer is present (fig. 15); otherwise, the oxygen radicals act as radical



(fig. 15)

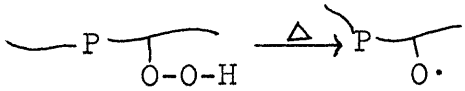
scavangers to cause chain termination by coupling with

short radicals (fig. 16). Although less efficient than



(fig. 16)

direct irradiation due to this radical deactivation, the crosslinking monomer is not irradiated. Theoretically, therefore, no homopolymer of crosslinking monomer should be formed; however, this homopolymerization is initiated by 1) hydroxyl radicals from heated hydroperoxides formed on the backbone (fig. 17) and 2) low molecular weight per-



(fig. 17)

oxides on the backbone which dissociate. To be suitable for preirradiation techniques a polymer must be stable 1) when heated to 150° C and 2) when subjected to the several megarads of radiation required for this technique--in comparison, only tenths of megarads of radiation are required for effective direct irradiation induced crosslinking.

The third irradiation technique, crosslinking by trapped radicals, is applicable to viscous polymers irradiated in an inert atmosphere below their glass transition temperature--T_g--so as to literally trap polymeric free radicals--crosslinking is initiated upon diffusion of crosslinking monomer to the trapped radicals (1). Again no crosslinking agent homopolymer theoretically should

be formed since the crosslinking monomer is not irradiated; furthermore, troublesome low molecular weight radicals which could initiate this homopolymerization, are not trapped at ordinary temperatures. Chain transfer can, however, yield this homopolymer. Although the same efficiency problems of a low concentration, short lifetime radical population encountered in the previous technique exists, a lower temperature can be used to initiate crosslinking, reducing the thermal stability requirements of polymerizable components.

The final method, irradiation induced crosslinking in emulsion systems, is attractive as the emulsion does not become too viscous at high conversion, making high crosslinking efficiencies possible.

E. Crosslinking Methods Utilized

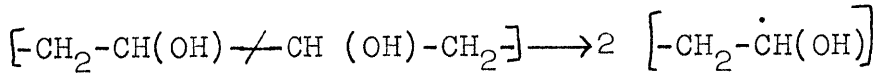
1. Redox System

One method of chemical inititiated crosslinking that might hold promise for PVA is the redox technique of Mino and Kaizerman (44, 45), using ceric ammonium nitrate as the initiating chemical.

The important parameters in the redox system are 1) reaction time, 2) reaction temperature, 3) PVA concentration, 4) crosslinking monomer concentration, and 5) the concentration of the ceric solution. The latter

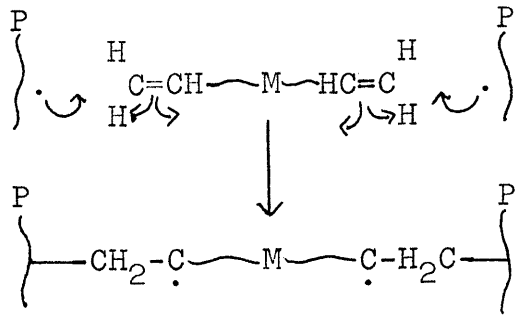
three parameters are probably of prime importance with variations of reaction time and temperature merely scaling the effects of variable concentrations.

Two points are of interest from work by Mino, et. al.: 1) reacting 1% PVA solutions they note no crosslinking in his successful grafts of monofunctional monomers to PVA--i.e., the PVA molecules do not crosslink themselves by formingPVA bridges; thus, any crosslinking resulting from the use of difunctional monomers would not be complexed by other crosslinking paths making correlations of results and variations in parameters simplified; however, pure PVA crosslinks might form in high concentration PVA solutions due to the decreased distance between radicals on PVA chains, and 2)a ratio of glycol groups in the PVA to the ceric ions produced, (Glycol)/(Ce^{3+}), greater than ten leads to fragmented ends from glycol scission (fig. 18) yielding block copolymers (45)



(fig. 18)

The following is a possible mechanism of formation of crosslinked PVA via difunctional vinyl monomers after radical formation on the PVA chain by oxidation reduction (fig. 19)



(fig. 19)

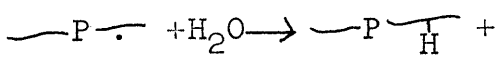
The free radicals on the monomer link can either couple with a hydrogen or hydroxyl radical or continue grafting by coupling with a polymer radical.

2. Irradiation Method

a. Rationale

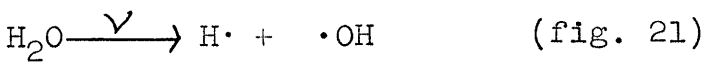
A second promising method of obtaining highly crosslinked high concentration PVA solutions is by the direct irradiation method in the presence of difunctional monomers. Early work by Bray and Bauer (12) of the synthetic cartilage group produced tough, hydrophilic, PVA networks--from 10% to 30% PVA--via direct irradiation without added crosslinking agents. One major reservation existed, however: the degree of crosslinking decreased with increasing PVA weight per cent thus limiting high degrees of crosslinking to low weight per cent PVA gels.

Chapiro (18) indicates that transfer to solvent (fig. 20) is virtually impossible due to the high dis-



(fig.20)

sociation energy of the O-H bond--120 kcal/mole. The very reactive hydrogen and hydroxyl radicals formed by radiolysis of water (fig. 21) readily abstract active hy-



(fig. 21)

drogens from the polymer molecule leaving free radical initiation sights. Thus, less aqueous PVA solutions see a decrease in solvent radiolysis resulting in less radical formation on the PVA backbones and hence less crosslinking.

An easy solution to this difficulty in obtaining highly crosslinked, high PVA concentration aqueous gels would be to increase the total dose above the 8 to 10 megarads used by Bray and Bauer, thus increasing both radiolysis of solvent and direct formation of radical initiation sights on the polymer chains (15) resulting in higher crosslinking. By the same token, however, chain scission is increased to such a degree that above a dose of approximately 10 megarads, brittle, non-elastic completely undesirable PVA networks result.

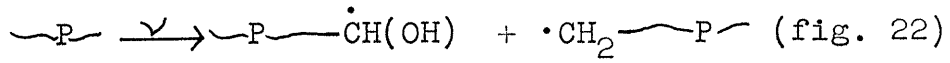
The investigation of the above problem thus conveniently fits the objectives of this thesis, for the use of crosslinking agents in high concentration PVA solu-

tions irradiated at 10 megarads or less could well enhance PVA crosslinking by increasing the number of paths available for two PVA backbone radicals to join.

b. General Considerations

The term, high energy radiation, includes two major subheadings of radiation, both of which may initiate crosslinking : 1) charged particles which can directly split an electron pair of a molecule producing two free radicals and 2) highly accelerated particles, charged or uncharged, which impart sufficient energy upon collision with a molecule to split the molecule into two free radicals. Free radical formation is not the only possible consequence of these collisions, however; the molecules could either ionize or dissipate the additional energy in light, vibrations, or some other energy form in returning to the ground state.

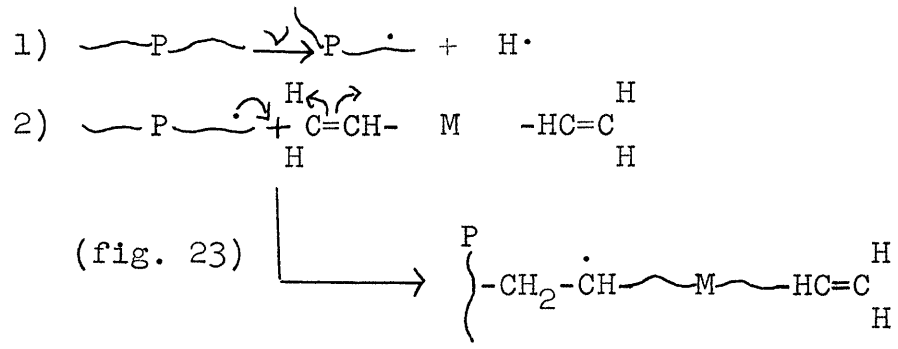
Irradiation of a polymer usually results in two simultaneous competing processes (9), 1) chain scission



(fig. 22)

(fig. 22 is an example) decreasing the molecular weight, and 2) free radical formation within the main chain increasing the molecular weight by grafting and possibly

crosslinking if the added monomer possesses two or more functional groups (fig. 23)--the radical now on the



(fig. 23)

grafted monomer could also finalize the crosslink by coupling with a radical on a polymer backbone.

Chain scission appears to be favored indirectly by 1) a polymeric chain structure in which the radical-producing extractable hydrogens are lacking--i.e., $-CH_2-CRR'-$ --and 2) irradiation of the polymer in air yielding insertion in the main chain of thermally unstable peroxide and hydroperoxide groups; once activated the oxygen acts as a free radical scavanger and can prevent crosslinking by coupling with low molecular weight radicals; scission is favored in both processes simply because the main chain lacks the radicals to initiate crosslinking (10). Recent evidence by Sakurada, et al, (52) however, indicates that the presence of oxygen during irradiation of PVA has no effect and might even enhance crosslinking. Further investigation is needed.

c. Variable Parameters

Easily varied parameters of a direct irradiation -induced crosslinking system include 1) total dose, 2) dose rate, 3) addition of crosslinking monomer, 4) PVA concentration, 5) the temperature during irradiation, and 6) added solvents, if any. Total dose, a very important variable determining the total number of grafting sites on the polymer chains and thus the network density, is measured in rads, the quantity of radiation required for one gram of the absorbing material to release 100 ergs of energy. Dose rate, measured in rads/unit time, has little effect on the gel formation (19). Polymer and crosslinking monomer concentrations are easily varied although low solubility of the crosslinking monomers in water may be a limiting factor. Evidence (13, 53) exists that irradiation of PVA at a temperature above its glass transition temperature produces best crosslinking results, as the high temperature promotes motion of the chains bringing reactive radicals closer together. Crosslinking monomers, by the same token, probably are more effective above the glass transition temperature of the polymer. PVA solvents in addition to or in place of water have proved successful in some irradiation-induced crosslinking systems: 1) Sakurada (51) using Cobalt 60 γ irradiation on PVA in methanol found tremendous

grafting with methyl methacrylate, and 2) Bernstein, et al, (8) also using a Cobalt-60 Y source but at low total dose, crosslinked an allyl methacrylate PVA solution dissolved in water and methanol. Chain transfer to solvent is undoubtedly involved in these two cases.

F. Criteria for Selection of Crosslinking Monomers.

The author's criteria for selection of crosslinking monomers involve four parameters: 1) water solubility, 2) activity of the functional groups, 3) molecular weight, and 4) the number of functional groups. Water solubility of the monomer is considered important so as to obtain intimate contact with the PVA and aid in crosslinking. Bernstein, Orban, and Odian's work (7) suggests that a non-water soluble crosslinking agent could effectively crosslink PVA if a solvent mutually miscible to water and the crosslinking agent--e.g., an organic agent in a methanol, water system--is employed. This route is unacceptable, however, due to the introduction of a toxic organic component into the system. Secondly, the functional groups of the crosslinking agent must be reactive to both crosslinking methods selected--the irradiation system and the redox system. The rate constants for chain transfer to solvent and to initiator--$k_{tr,s}$ and $k_{tr,i}$--should be low to prevent radical transfer

to solvent or initiator with resulting homopolymerization. Selecting crosslinking agents of varying rate constants of chain transfer to monomer ($k_{tr,m}$)--i.e., varying degrees of monomer-monomer bonding as compared to monomer-polymer bonding--might well affect the average interchain length. Crosslinking agents with both symmetrical and non-symmetrical functional groups test the relative reactivities of functional groups. Third, crosslinking agents of different molecular weights, or more specific, variable backbone length, might create networks of varying degrees of tightness. Finally, di-, tri-, and higher multi-functional monomers should have an increasing effect on the tightness of the network.

G. Swelling Theory

A polymeric crosslinked network placed in a pure solvent of the uncrosslinked polymer will swell as the polymer absorbs the solvent in an attempt to dissolve (30, 47); however, the mixing forces are eventually balanced by the force of retraction of the crosslinked network leaving the network insoluble. This insolubility is quite evident if the crosslinked polymer is heated to its glass transition temperature--any crystallites formed at lower temperatures will now dissolve and leave the crosslinked network which remains intact due to the

restraining bridges.

Two important variables of the swelling of crosslinked polymers are the solvent temperature and the solvent, the effect of both expressed by the χ factor, a dimensionless quantity characterizing the interaction energy per solvent molecule divided by kT (k is the Boltzmann Constant and T is the system temperature). Negative χ factors characterize good polymeric solvents while positive χ factors indicate poor solvents (47).

Swelling theory of a lightly crosslinked network at swelling equilibrium, well developed by Flory (30), produces a complicated equation containing three primary unknowns: M_c, the average molecular weight between crosslinked junctions, the χ factor, and v(2m), the volume fraction of polymer at equilibrium in the pure solvent, which is readily calculated from swelling measurements. Although the χ factor for aqueous PVA alone is known, the addition of crosslinking monomer alters this quantity making M_c, a quantitative measure of crosslinking, unattainable for these crosslinked systems. All swelling data are therefore taken at 30° C and compared to a standard of PVA swollen in pure water at 30° C yielding relative swelling and hopefully relative M_c values.

III. APPARATUS AND PROCEDURES

A. Reactants

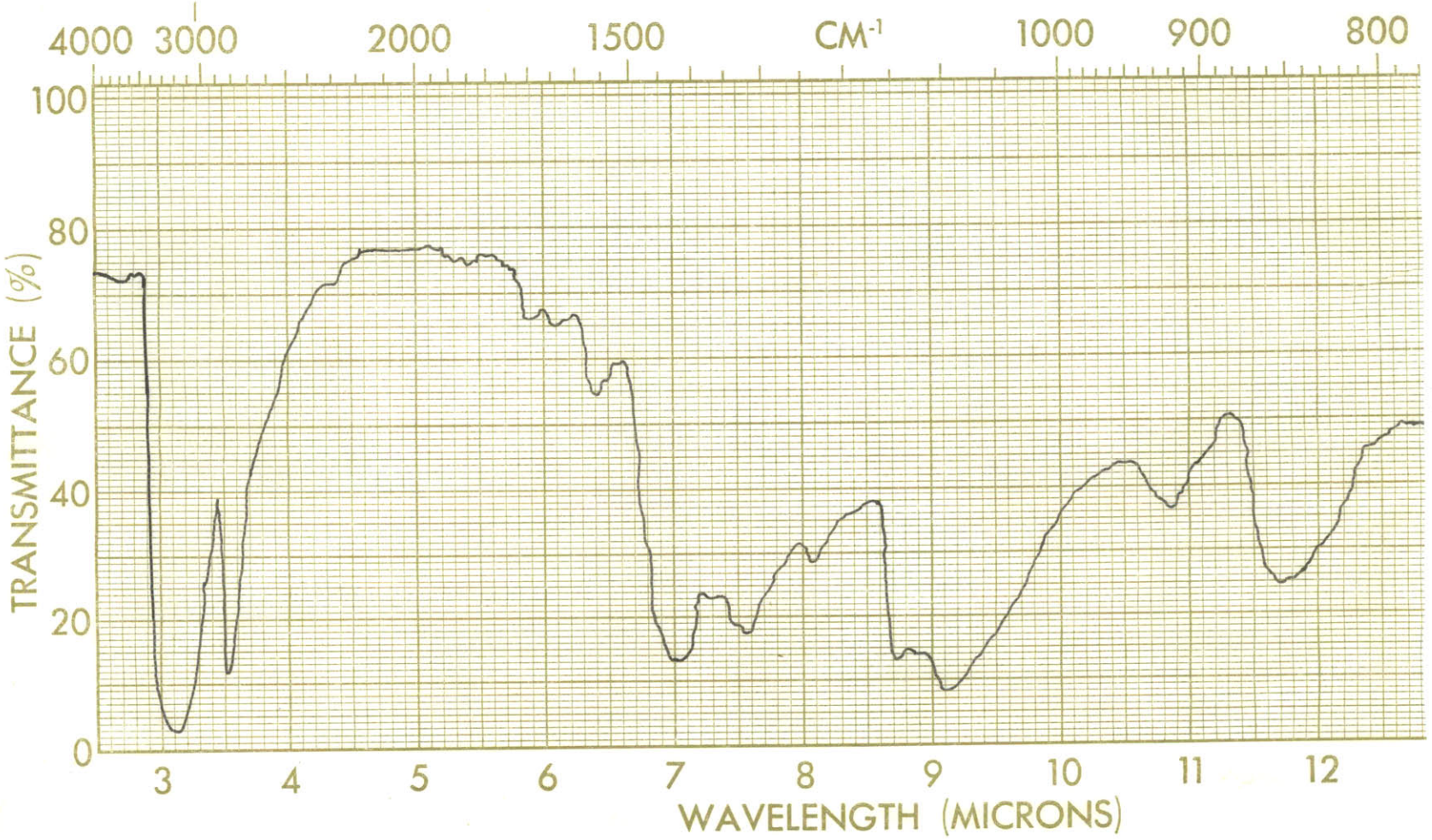
1. PVA

Chemical and physical properties (28, 48) of PVA--its structural unit is illustrated in fig. 24--made it a very advantageous material to use in this project. To begin with, high quality PVA with a wide range of molecular weights--up to about one million--was available as PVA Elvano from E. I. Du Pont De Nemours and Co., Inc.; an extensive IR analysis of Elvanol (35) revealed no indication of acetal, peroxide, or carboxylic acid groups and less then .1% by weight of carbonyl groups, as witnessed by the IR spectrum (6) in figure 25; needless to say, the purity of Elvanol greatly simplified the explanation of chemical mechanisms. As to fulfilling the medical criteria of a synthetic cartilage: 1) as a water-soluble polymer, a crosslinked PVA material would readily swell in vivo; 2) charged groups had previously been grafted to PVA (32); and 3) PVA hydrogels exhibited the ultrafiltration capabilities necessary for the synthetic cartilage to concentrate hyaluranate at the surface when stressed.

$[-CH_2-CH(OH)-]$

(fig. 24)

The specific grade of Elvanol used--72-60, with


4000 3000 2000 1500 CM-1 1000 900 800
100
80
60
40
20
0
TRANSMITTANCE (%)
3 4 5 6 7 8 9 10 11 12
WAVELENGTH (MICRONS)

(fig. 25)

a molecular weight bewween 170,000and 220,000 (7)--was 99.0 to 99.8% hydrolyzed vinyl acetate (27)--fig. 26--the parent of all commercially synthesized PVA.

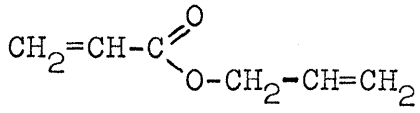
$$\{CH_2\text{-}CH(OCOCH_3)\}$$

(fig. 26)

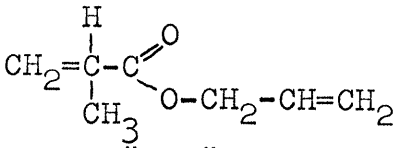
2. Crosslinking Agents

Table I lists the important properties of, among others, the five selected crosslinking agents: 1) water-soluble allyl acrylate obtained from Polymer Research Corp. of America, 2) water-soluble allyl methacrylate, also obtained from the Polymer Research Corp. of America, 3) N'-N'-methylene bis acrylamide obtained from Eastman Laboratories, 4) diallylamine obtained from Polysciences, and 5)tetra ethylene glycol dimethacrylate obtained from Borden's Monomer-Polymer Laboratories. These five monomers (fig. 27) are abbreviated AA, AMA, MBA, DAA, and TEGDM. The first two allylic monomers were initially obtained from Sartomer Resins, Inc. in a water insoluble form prior to discovery that a water-soluble form, only slightly soluble at room temperature, however, existed. Data sheets indicated that TEGDM also was water insoluble, but it was found to be approximately the same limited solubility as allyl methacrylate. MBA, the only monomer

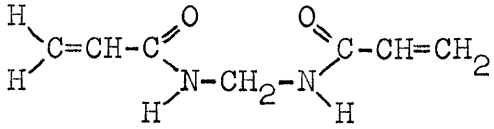
(fig. 27)



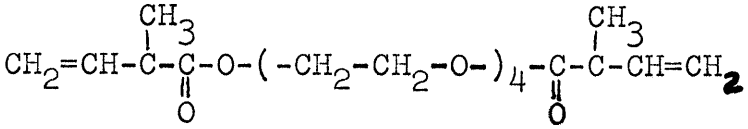
"AA"



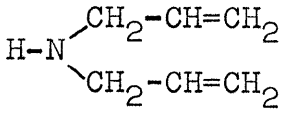
"AMA"



"MBA"



"TEGDM"



"DAA"

supplied in solid form, was second in water solubility only to DAA. Monomers more water-soluble than a few per cent had been desired to attain a higher crosslinking agent concentration in the reacting PVA samples. The two acrylate monomers served two purpose : 1) they both were unsymmetrical with respect to their functional groups and 2) the allylic and acrylic groups varied markedly in reactivity, the acrylic group being more reactive and the allylic group possessing an extremely high transfer to monomer constant, C_M. Due to the close chemical similarity of these two monomers, similar results were expected from them; however, they both were water-soluble, as opposed to most other crosslinking monomers, and similar results would, in the least, be reassuring. The other three monomers were all symmetrical with respect to their functional groups; TEGDM had the highest molecular weight and was the longest monomer of the five.

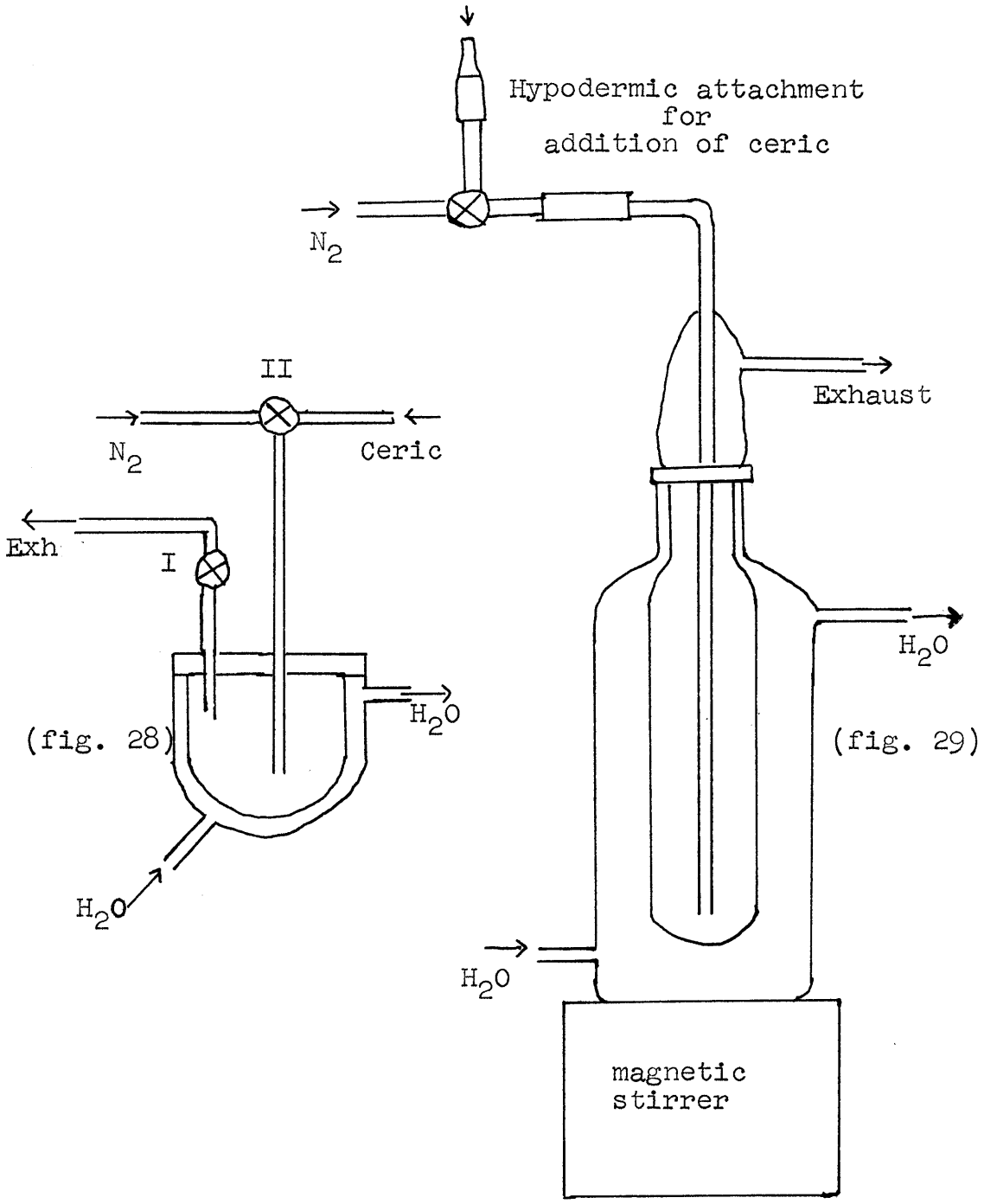
B. Redox System

The ceric ion based redox system used to attempt chemical crosslinking of PVA closely followed Mino and Kaizerman's procedures (44) The redox agent was .1 M ceric ammonium nitrate in 1.0 M nitric acid. All reactions were performed on PVA Elvanol 72-60 at 20° C. Procedures to eliminate oxygen--e.g., initial degassing of the reac-

tants, air-tight reactors, and hypodermic injection into the reactor--improved steadily. After one hour, the reaction was quenched by cold acetone which precipitated the gross polymer, an off-white lumpy mass. Ten to twelve passes of one hundred ml. volumes of acetone through the sample while in a buchner funnel removed excess ceric solution and unreacted monomer. Heating of the product at 90° C overnight in distilled water removed any crystallites while testing for crosslinking.

The reactants, products, and observations of all redox runs are listed in Table II.

The initial redox runs, numbers one to five, were performed to qualitatively determine the viability of the ceric ammonium redox system as a means of crosslinking PVA via difunctional monomer bridges. A 10% PVA aqueous solution was selected arbitrarily while the crosslinking agents used were MBA and TEGDM. No attempts were made to degas initially any of the reactants. The two monomers were added directly to the reactions without regard for their water solubilities--see Table II--MBA was about 3% soluble while TEGDM was about .5% water soluble. The reaction vessel (fig. 28) for runs one through five was an Ace Glassware jacketed dewar condenser, 70 mm by 90 mm, and approximately 300 cc in volume. Two holes cut into a fitted cork sealed with Krylon acrylic spray were used


Hypodermic attachment
for
addition of ceric
N_2
Exhaust
II
N_2
Ceric
Exh
I
H_2O
(fig. 28)
H_2O
H_2O
(fig. 29)
H_2O
magnetic
stirrer

as 1) a combined nitrogen, ceric solution inlet port extending to the vessel bottom, and 2) an exhaust port extending just below the cork level. The ceric solution entered via a calibrated burret connected by tygon tubing to valve II. After adding the PVA and crosslinking monomer, if any, the reactor was sealed and the following procedures begun: 1) the water bath was maintained at 20° C for approximately thirty minutes prior to the reaction; 2) a vacuum was pulled on the sealed vessel for about five minutes--surface bubbling of the PVA while under vacuum indicated degassing; and 3) pre-purified nitrogen was slowly bubbled through the reacting mass. Halting the purge momentarily, the ceric was added via the nitrogen line to initiate the reaction. Initial foaming was reduced by the addition of GE Silicone Antifoam #72 and reduction of the nitrogen flow. The addition of ceric solution on run four via a hypodermic proved simpler and faster, while a sparger added for better mixing, was a failure as such for it quickly clogged in the viscous mass.

A 150 ml. jacketed reaction vessel with a ground glass fitting (fig. 29) was suitable for use with a magnetic stirrer and was used for all redox runs after number four.

To obtain better acetone extraction, the amorphous products from runs two through five were cut into small

pieces greatly increasing the exposed area.

In runs six through ten, the PVA was degassed by placing the reactor containing the dry preweighed PVA in a vacuum dessicator in a nitrogen glove box. Pulling a mechanical vacuum and then venting the dessicator with nitrogen, left the PVA degassed. After adding, under nitrogen, distilled water, degassed by twenty minutes of boiling, the reactor was sealed (two screw clamps sealed the rubber tubing attached to the inlet and exhaust stems), removed from the glove box, and placed at 90° C to dissolve the polymer. The ceric ammonium nitrate was directly degassed in a vacuum dessicator by a mechanical vacuum.

Run number six, another control to determine the effect of the redox system on PVA alone, used the above degassed reactants and a more oxygen-free system than that in run one. Mixing was enhanced by using a less viscous PVA solution--5%by weight PVA. After connecting the sealed reactor,containing the PVA, antifoam, and magnetic stirrerto the nitrogen source and water bath, the system was stirred and purged for forty-five minutes to allow it to equilibrate at 20° C. After injecting the ceric by hypodermic into the reactor via the nitrogen line, it was noted that approximately one ml. of ceric solution remained in the syringe and its fittings.

The magnetic stirrer worked well for the 5% PVA solution in run six, so solutions of 9 and 13% PVA were prepared for run seven.

To increase output, three of the 150 ml reactors were connected to the water bath in countercurrent series for run eight. A set of three "T" valves beyond the hypodermic, nitrogen junction, allowed simultaneous nitrogen purging of all three reactors while selectively being able to inject ceric into one.

Run eight was a continuation of number six using a ten-fold increase and a ten-fold decrease in ceric concentration. To avoid oxygen contact the following indirect method was used to weigh out PVA from pre-dissolved PVA sealed under nitrogen: 1) the sealed vessel, stirring bar, plus antifoam weight was determined; 2) after adding the degassed PVA under nitrogen to a line indicating approximately forty cc's, the reactor was again sealed and weighed. From the difference of one and two, the amount of catalyst was determined to maintain a ceric ion concentration of .0116 moles/liter.

The procedures of run eight were maintained in run nine, which used two crosslinking agents, MBA and TEGDM, the latter at two concentration.

A 15% PVA solution was used in run ten with MBA, DAA, and AMA as crosslinking agents. Due to reactor

limitations, the amount of each agent added was only 5% by weight of the PVA (dry weight)-monomer mixture.

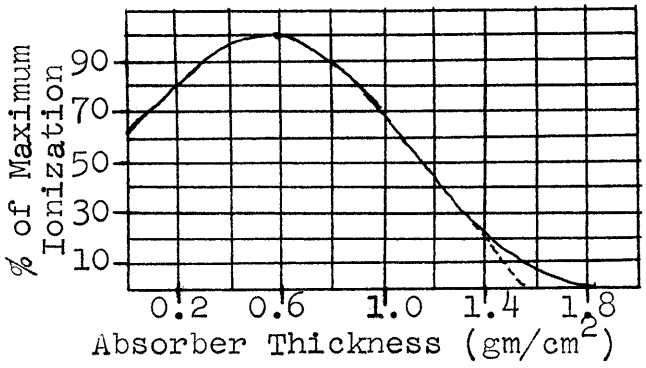
As the stirring bars were frozen in the viscous PVA, the ceric was not being mixed. After opening each reactor and stirring the contents with a pipette, through which nitrogen was flowing, the ceric was evenly distributed, decreasing the PVA viscosity thus unthawing the stirring bars.

C. Irradiation System

1. Selection of Radiation Source

Two availabee irradiation sources--the Cobalt 60 γ source and the 3 M.E.V. β accelerator under the supervision of Dr. Kenneth Wright at the MIT High Voltage Laboratory--were readily available for irradiation-induced crosslinking. The former, having a constant dose rate of 4,700 rads/min, required well over a day to achieve dose levels in the megarad range. However, the penetrating γ rays allowed samples to be sealed under vacuum in glass tubes while maintaining homogenouus irradiation, thus completely eliminating complications from oxygen during irradiation. For a number of reasons, however, the β accelerator was used exclusively: 1) most important, the variable and extremely high dose rates--from 10,000 to 200,000 rad/sec--gave total doses of sev-

eral megarads in a matter of minutes; 2) the radiation could be focused, unlike the diffuse, scattered radiation from a radioactive source; 3) it could be turned on and off at will thus requiring no extensive shielding in which to store the source. Two disadvantages of the β accelerator stemmed from its limited penetrating power--about 1 to 2 cm/unit density, depending on the energy of the particles: 1) the samples could not be sealed in thick evacuated tubes, thus necessitating other precautionary measures of maintaining the samples in an inert atmosphere, and 2) a dose to depth limitation existed--i.e., the true dose absorbed by a material was some fraction of the actual dose, depending on the thickness,of the absorbing material. This fraction, or per cent ionization, is plotted vs. range in the absorbing material--gm/sq cm--for a 3 M.E.V. electron beam (fig. 30). Dividing this range by the density of the absorber material--essentially unity for aqueous PVA gels--gives the range in cm; thus, a sample of thickness between .5 and .6 cm is 100% ionized--i.e., it absorbs the actual dose irradiated. The thermal side effects of the high



(fig. 30)

energy β irradiation also had to be counteracted to prevent increased polymerization due to rising temperatures during irradiation.

Small--15 mm by 50 mm--covered, round, culture dishes proved to be excellent containers for the irradiation samples: 1) the samples were a convenient size and shape for the swelling tests, and 2) a ten gram sample was roughly 0.5 cm thick making dose to depth corrections unnecessary.

All liquid crosslinking agents--AA, AMA, DAA, and TEGDM--were degassed via continuous freeze-thaw cycling. Preweighed solid reactants--i.e,, MBA and PVA--were degassed in a vacuum dessicator inside a glove box prior to being dissolved in boiled, degassed water.

Two methods were used to add the crosslinking monomer--done under nitrogen--to the PVA: method 1) the total dissolved solution of crosslinking monomer and water was added directly by pipette to insure complete wetting of the PVA; and method 2) after dissolving the sample at 90 °C with only half the total solvent--excluding crosslinking monomer--a solution of all the crosslinking monomer and the remaining water was added and the sample was set aside to swell for 24 hours. Method one introduced a higher total crosslinking agent concentration into the sample, whereas method two avoided exposure

of the crosslinking monomer to the possible thermally initiating effects of 90 °C.

2. Procedures and Apparatus

A sample was doubly sealed with saran wrap while still inside the glove box prior to being heated to 90 °C to dissolve the PVA. After using an elastic to secure a taut saran window over the bottom dish, the cover was added and the two piece culture dish was again sealed in saran and then secured with two elastics. Saran wrap was used as a sealant because of its impermeability and its shrinking property upon heating, thus forming an excellent seal. To check the effectiveness of this double seal, twelve weighed, sealed samples were heated to 90 °C for 12 hours while one sample was kept at room temperature as a control. Final weights were then taken to determine any water loss.

Prior to irradiation, a .25 mil mylar sheet was secured over the bottom dish. Acting as a window through which radiation could pass, the thin mylar could neither impede β rays passing through it nor disintegrate as saran would under β irradiation. With the glass covers in place, the samples were loaded into large crystallizing dishes, which were then sealed with saran and left in the glove box until irradiation.

An ice bath in a large crystallizing dish maintained the samples at 0 °C during irradiation. Four uncovered, mylar sealed samples were clustered in the center of each crystallizing dish with ice cubes around the edges keeping them in place. The samples were then irradiated by placing the ice baths on a conveyer belt which moved at a constant speed under the β emitting window. The belt speed determined the dose given the samples, the maximum being five megarads. Multiple passes were required for higher doses. Excess water was removed from the baths and fresh ice added after each pass as the high energy irradiation rapidly melted the ice. The irradiated samples were returned to the lab and refrigerated if swelling analysis could not be started immediately.

3. Variables Investigated

Four separate series of PVA samples were irradiated varying the total dose, crosslinking agent concentration, and the PVA concentration as indicated in Table III. The selection of variable dose levels of 3, 5, 8, 10, and 15 megarads was based on parallel work by Bray (11)--these doses centered around the 8 to 10 megarad dose level producing the optimal gel characteristics of flexibility, tensile strength, and overall durability.

When constant, the crosslinking agent concentration was always the maximum concentration which solubility limitations would allow. When varied, the concentration was diluted in increments from this maximum. A 20% PVA aqueous solution was arbitrarily selected for initial work.

The reactants of the samples of each series are tabulated in the indicated tables.

a. Series A (Table V)

After selection and degassing of four possible crosslinking monomers, AA, DAA, AMA, and MBA, 20% PVA samples were prepared to investigate the effect of the varying concentrations of the added crosslinking monomers. The crosslinking agents were added by method one, discussed in the previous section, using a serial dilution technique (see Appendix A) to obtain an approximately five-fold concentration range. The volume of crosslinking agent added reflects the calculated density (Table IV). All samples were irradiated with ten megarads--two five megarad passes. Samples A-13 to A 16 were run as controls to check for any noticeable effect of degassing the crosslinking agents while the two PVA runs, A-17 (solvated in degassed water) and A-18 (solvated in non-degassed water) were to check the effects of oxygen in the water.

b. Series B (Table VIII)

The B Series was run to determine the effect of a variable total dose on 20% PVA samples containing a constant concentration of the following crosslinking agents: AA, AMA, DAA, MBA,and TEGDM.Using method two to add the crosslinking agents, a sample calculation of the total weight per cent crosslinking agent is given in Appendix B.

c. Series C (Table XI)

This series was a further study of MBA on PVA crosslinking by combining the variables--total dose and crosslinking agent concentration--of Series A and Series B. The procedures of Series B were followed with initial monomer concentrations ranging over two decades, from 0.03% to 3.0%.

d. Series D (Table XIV)

Series D, following the procedures of Series A, was run to determine the effect of crosslinking agents on the swelling ratio of PVA at several concentrations--from 5% to about 35% PVA. The crosslinking agents were AMA, MBA, and TEGDM. A technical problem arose in maintaining a constant total weight per cent of crosslinking agent with varying weight per cent of PVA. From equation

$$\text{total wt.\% C.L. agent} = \frac{\left[\text{Weight of added solvent}\right]\left[\text{C.L. agent wt.\% of added solvent}\right]}{\text{PVA dry weight} + \text{Weight of added solvent}} \quad (1)$$

(1) it was obvious that as solvent was added to obtain more dilute PVA solutions, the total weight per cent of crosslinking agent would increase unless the crosslinking agent wt.% of added solvent was decreased by an appropriate amount (see Appendix C).

D. Swelling Tests

Swelling tests were designed to measure the swelling ratio q, the ratio at a fixed temperature of the volume of polymer in the swollen state at equilibrium to the volume of polymer in the relaxed or initial unswollen state.

To determine the swelling ratio of a network, several weights were determined: 1) W(OA), the weight of the sample in air prior to swelling, 2) W(OW), the weight of the sample in 30 °C water prior to swelling, 3) W(SA), the weight of the sample in air at swollen equilibrium, and 4) W(SW), the weight of the sample in 30 °C water at swollen equilibrium.

After irradiation, a sample was carefully removed

from its container and weighed in air, W(OA). Then, hanging the sample from a hook into a beaker of 30 °C water, W(OW) was recorded. Immediate swelling--a water uptake of about 0.0001 gm/sec of all non-floating samples--was noted.

After heating the samples at 90 °C in distilled water to extract any crystallites which would effect the swelling, the samples were placed in fresh distilled water and left to swell.

Measurements every two days of the swollen weight in air of initial gels showed that the gels reached an equilibrium state after about six days. Thus, after six days the samples were placed in a 30 °C oven for two additional days to reach final equilibrium--30 °C was selected in order to compare any data with that of swollen pure PVA, previously determined at 30 °C.

After removal of the equilibrated sample from the 30 °C container, excess surface water was absorbed onto a paper towel and the weights in air and water were recorded as before. Minute evaporation on the order of 0.0001 gm/sec was evident of swollen samples weighed in air.

With all measurements recorded, the samples, in aluminum dishes, were placed inside a vacuum oven maintained at 60 °C and maximum vacuum for two to three days to dehydrate the samples. The weight of the final product

was the dry polymer weight, W(D).

IV. RESULTS AND DISCUSSION

A. Redox System

Table II lists the reactants, products, and results of the redox system experiments. The insolubility of the product at 90 °C is an excellent indication of a crosslinked network, the extra bonds keeping the polymer chains from separating. The ceric concentration in moles/liter is the ceric ion concentration in the reactor. Mino (45) reports that the glycol concentration in PVA Elvanol 70-05, about one-tenth the molecular weight of Elvanol 72-60 but essentially the same composition, is 5.7×10^{-4} moles/liter; if a similar concentration in Elvanol 72-60 is assumed, Mino's criteria of $[\text{Glycol}] / [Ce^{+++}]$ less than ten to avoid glycol scission and resulting block copolymerization requires a ceric ion concentration greater than 5.7×10^{-5} moles/liter. The ceric ion concentration in all runs was greater than this amount.

Run one of the initial five redox runs was a control for any crosslinking without a difunctional vinyl monomer--i.e., the PVA chains forming their own crosslink bridges. The negative results were expected, for Mino and Kaizerman (44) had detected no crosslinking in their redox systems of PVA and monofunctional vinyl monomers, the equivalent of run number one, for any crosslinking would have to be via PVA bridges.

Runs two through four seem to give credibility to the redox system as a PVA crosslinking method--the yields indicate monomer incorporation into the polymer of 30% and 100% for TEGDM and MBA, respectively. A solubility test at 90 °C was not performed on these runs to check for crosslinking. Thus these runs could merely indicate the entanglement of two homopolymers and absolutely no crosslinking. Run number five, a repeat of run four but with increased precautions to maintain an inert atmosphere, yielded an insoluble, crosslinked network. The crosslinking monomer was added to the reaction without regard for water solubility, later considered important for monomer-polymer interaction. As it turns out, the TEGDM, at 0.86 total wt. %, was only in slight excess of its water solubility at room temperature (.54% by weight). The MBA, however, added on a one to one basis with PVA, was at a concentration--about 8.7%--almost three times its water solubility at room temperature (about 3.0%). Although one might think saturated solutions of these crosslinking monomers would form in the PVA, this was not the case, as the PVA was too viscous for these monomers to mix and readily dissolve. Heating the resulting suspensions might well have dissolved the monomers, but the heat could also have initiated polymerization of the crosslinking agent. Thus for further redox runs and all

irradiation runs as well the crosslinking agents were added in aqueous, dilute solutions.

A yield was not taken on run number five as the crosslinked product was left to swell in water to attempt a swelling analysis. As no analytical methods could be conceived for obtaining swelling data on this amorphous mass, the redox system was temporarily abandoned in favor of irradiation techniques.

In hopes of obtaining more quantitative results, the redox method was again investigated. Many sources of inaccuracy encountered on the initial runs had been solved: 1) foaming was effectively eliminated with GE Silicone Antifoam #72; 2) the crosslinking monomers were dissolved in water for better mixing and hence better monomer-polymer contact; 3) degassing tachniques--vacuum dessication under nitrogen and freeze-thaw methods--from the irradiation method were employed; 4) an air tight and well purged system was used; and 5)the new reactor could be set on a magnetic stirrer for better mixing.

Run number six was designated as the control run, like number one, utilizing the above information. Although the magnetic stirrer worked well for this 5% PVA solution, the 9% and 13% PVA solutions of run seven were abandoned as being too viscous to be stirred. An easy solution to this viscosity problem would be to raise the reaction

temperature affecting reaction rates as well.

Runs 8"a"and "b" hosted a ten fold increase and decrease respectively in ceric concentration with respect to run six with no apparent effect in the result--no crosslinking. It was interesting that 8 "b" with its high ceric concentration turned from an initial black to a dark brown instead of the normal dull red to clear for a ceric concentration of about 0.01 moles/liter--the PVA was undoubtedly completely oxidized since the acetone extracted filtrate was orange colored,indicating the presence of active nonreduced ceric.

A higher concentration of PVA solution might be the answer to some of these problems, for it is possible the PVA chains were simply too dilute and scattered to allow free radical sites on different chains to be joined, whether it be via other PVA chains or through difunctional vinyl monomers.

Run nine again showed signs of PVA crosslinking by MBA, this time added in solution as opposed to the previously discussed bulk additions. This great increase in the PVA to monomer ratio--ten to one or greater in these runs as compared to about one to one in runs two and four--could account for the only slight crosslinking with MBA and no crosslinking with TEGDM. Return to bulk addition of MBA seems the best alternative for future work.

A move to a 15 % PVA concentration in run ten, keeping the ratio by weight of PVA to crosslinking monomer at approximately twenty to one, produced some crosslinking with MBA. The problems encountered due to the high viscosity of this relatively low concentration PVA solution suggests that this redox system is incapable, without major revisions, to produce the highly concentrated PVA gels desired.

B. Swelling Analysis

Three volumes are readily calculated from the swelling data: 1) V(R), the relaxed polymer volume after irradiation, 2) V(S), the swollen polymer volume at swelling equilibrium, and 3) V(P), the dry polymer volume, the three volumes differing mainly from uncoiling or tightening of the polymer chain and branches due to solvent gain or loss, respectively.

V(R) andV(S) are based on bouyant density, or the volume displaced by the initial and the swollen gel. The weight difference between air and water is the weight of the solvent, water in this case, displaced. The volume displaced, the desired quantity, is simply the solvent weight displaced divided by the solvent density, the latter being a function of the system temperature (the density of water at 30 °C = 0.996 gm/cc):

$$V(R) = \frac{W(OA) - W(OW)}{.996 \text{ gm/cc}} \qquad (2)$$

$$V(S) = \frac{W(SA) - W(SW)}{.996 \text{ gm/cc}} \qquad (3)$$

The volume of dry polymer, V(P), is merely the weight of the dry polymer divided by its density --1.269 gm/cc for crystalline PVA (50):

$$V(P) = \frac{W(D)}{1.269 \text{ gm/cc}} \qquad (4)$$

Volume fractions, the fractional volume of the desired state, either relaxed or swollen, occupied by the polymer are calculated as follows:

$$v(R) = \frac{V(P)}{V(R)} \qquad (5) \qquad\qquad v(S) = \frac{V(P)}{V(S)} \qquad (6)$$

The fractional volume of the swollen gel occupied by the polymer at equilibrium --v(2m)--is

$$v(2m) = \frac{v(S)}{v(R)} = \frac{V(R)}{V(S)} = \frac{1}{q}$$

All swelling ratios in this work are calculated as using the recorded weights, i.e.

$$q = \frac{W(SA) - W(SW)}{W(OA) - W(OW)}$$

with volumes and volume fractions used as checks.

C. Irradiation System

1. General

The strong dependence of irradiation-induced crosslinking of aqueous PVA solutions on the radiolysis of water was a central issue of this work. The enhancement of direct radical formation on PVA chains from hydrogen extraction by these hydrogen and hydroxyl radicals decreased steadily with decreasing water concentration and hence decreased water radiolysis.

The addition of difunctional monomers to concentrated PVA solutions was proposed to enhance crosslinking, not by increasing the backbone radical population but by providing more paths by which these radicals could join.

Allylic monomers--AA, AMA, and DAA--possess properties of interest to their crosslinking nature. Two routes of reaction are open to an allylic monomer and a free radical (31): a) chain propagation (fig. 31) in

$$M\cdot + CH_2{=}CH\text{-}CH_2OCOCH_3 \longrightarrow M\text{-}CH_2\text{-}\dot{C}H\text{-}CH_2OCOCH_3$$

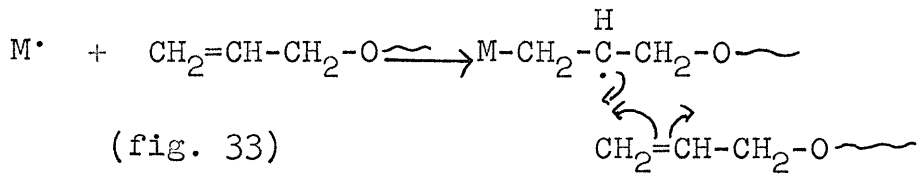
(fig. 31)

which the radical remains active and b) extraction of a hydrogen atom (fig. 32) producing a resonance stabilized

(fig. 32)

$$M\cdot + CH_2{=}CH\text{-}CH_2\text{-}OCOCH_3 \longrightarrow M\text{-}H + \dot{C}H_2{=}CH{=}\dot{O}COCH_3$$

inactive molecule. Allylic monomers have extremely high chain transfer to monomer rate constants (2) via route one--i.e., upon radical initiation, allylic monomers rapidly homopolymerize (fig. 33)



(fig. 33)

The water loss due to evaporation during heating of the PVA samples when dissolving had a range of 0.2 gm to 0.4 gm for 12 samples; this meant the final weight per cent of PVA was 20.6% $\pm$ .2--the double seal about the sample was fairly effective.

The charts and tables referred to for each of the following series present the data and results for each.

2. Specific

a. Series A (Tables V-VII; Chart I)

Bubble formation from gas evolution during irradiation created some problems in data taking. W(OW) was impossible to determine accurately as the networks either floated or were bouyed significantly by the trapped gas. After reviewing Bray's data (11) for irradiation runs of PVA under similar conditions but containing fewer bubbles, W(OW) was estimated at 0.4 gm. Heating the samples

to 90 °C to eliminate crystallites also effectively removed the gas bubbles which could easily diffuse out at this elevated temperature.

The samples containing DAA met with nothing but failure. When initially heated to 90 °C with the PVA, the DAA reacted with the saran disintegrating the latter. After irradiation the two higher concentration DAA samples completely dissolved when reheated to 90 °C, while the sample of only 0.5 total wt. % DAA remained a gel but did swell substantially. A possible explanation is that 1) hydrogen radicals were abstracted by the PVA radicals from the abundance of allyl groups thus killing many radicals on the main chains; the resononce-stabilized allyl product also was inactivated; and 2) other PVA radicals attacked the allylic groups by chain transfer producing PVA chains with pendant allylic branches greatly favoring lengthening of these branches via allylic homopolymerization over crosslinking due to the high transfer constant to monomer. The slight crosslinking of the sample of low total concentration DAA resulted from some PVA to PVA grafting and eventual crosslinking.

As hoped and expected, the AA and AMA samples yielded similar swelling results--swelling increased with the weight per cent of total crosslinking agent--Chart I--probably due to some inhibition of crosslinking by the

allylic monomers. It is likely that the PVA radicals attacked the reactive acrylic groups while the allylic end of the monomer homopolymerized with eventually some terminating in the resonance-stabilized form and some coupling with PVA radicals forming long crosslinks. Less PVA crosslinking than expected could occur due to these excess radical scavanging acrylic groups. With increasing AMA and AA concentration, more long branches and long monomer crosslinks were formed and fewer tight PVA crosslinks were produced thus increasing the swelling capacity.

The difunctional symmetric monomer MBA appeared to be attacked by PVA radicals from both ends, for it had a low transfer to monomer rate constant ($k_{tr,m}$)--(fig. 19). MBA thus seemed to enhance the crosslinking of PVA as fairly short chains were added. Although MBA could not homopolymerize as fast as the allylic monomers--C_M for an allylic group is some 500 times greater than for an acrylamide group--some homopolymer formation was possible.

A comparison of the swelling factors of first, samples containing degassed crosslinking monomer (A-1, A-4, and A-10) to samples containing non-degassed crosslinking monomer (A-13, A-14, and A-15), and second, the PVA sample dissolved in degassed water (A-17) to that dissolved in non-degassed water (A-18) yields little variation in both cases. A more thorough study of the effect of oxygen on

these systems should be undertaken, considering a controversy does exist.

b. Series B (Tables VIII-X; Chart II)

Similar results were again noted for the samples containing AA and AMA. The very high swelling ratio for low dose samples--approximately 1.5 to 2 times greater than the respective PVA sample--is explained again by the free radical scavanging of the acrylic group and the high transfer to monomer constant and resonance-stabilized termination of the allylic group;

At low doses--viz., 3 megarads--the MBA sample showed approximately a 26% tighter network than the corresponding PVA sample, all due to the additive effect of MBA crosslinks to the PVA crosslinks.

The results of the extremely long difunctional symmetrical monomer, TEGDM, were quite similar to those for pure PVA. The long TEGDM molecule was probably incorporated into the network but did not affect its tightness, as the TEGDM molecule was the same length or longer than the average crosslink, having a molecular weight of M_C. If the factor could be determined for these PVA, crosslinking monomer systems, M_C could be calculated increasing the understanding of systems like the above.

The asymptotic values of the swelling ratio with

increasing dose resulted as 1) the coupling mechanism of PVA radicals, the number of which increased with dose, began overwhelming any crosslinking monomer effect, and 2) the polymer became so viscous that excess PVA radicals initiated by electron bombardment were essentially frozen in place unable to react.

The following are reference data for pure 20% PVA Elvanol irradiated at 0 °C obtained from Bray (11) and plotted on Chart II as a reference for Series B.

Dose, mrads	q
3	2.7496
5	1.891
8	1.489
10	1.390
15	1.163

c. Series C (Tables XI-XIII; Chart III)

At low doses--3 megarads, in particular--the expected spread of MBA concentrations from high to low for increasing "q" was noted. The almost exact landing of the lowest concentration MBA sample--0.012% of the total weight--indicated this concentration of MBA was too dilute to cause enough crosslinking to effect the PVA crosslinking. The remaining data points follow a general asymptotic trend but are buckshot locally and thus no further conclu-

sions can be drawn.

This data indicates the possibility of using MBA to crosslink high concentrations of PVA at low doses.

d. Series D (Tables XIV-XVI; Chart IV)

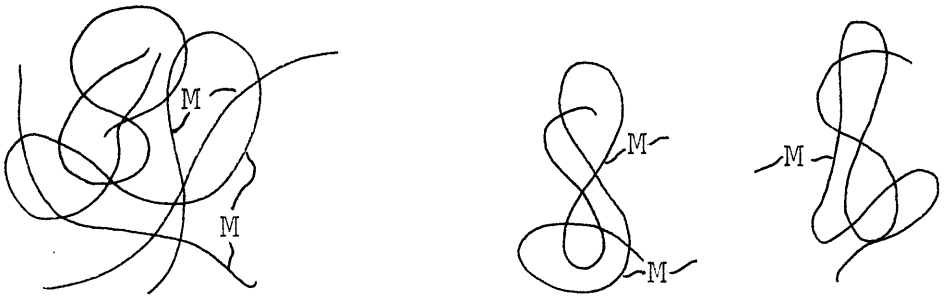
Chart IV accurately illustrates the decreased crosslinking--and increased swelling--of PVA with increasing PVA weight per cent. MBA seemed to counteract this process above 22% PVA by providing crosslinking paths. As the PVA concentration decreased below 20%, however, the radical density also decreased. Thus it is likely that as the backbone radicals on these PVA chains became increasingly separated, fewer MBA molecules could crosslink; instead, only one functional group could graft, killing radicals in the process and producing PVA chains with pendant MBA branches (fig. 35)--"M" indicates MBA molecules

(Network greater than 20% PVA) (Network less than 20% PVA)

(fig. 35)

TEGDM again had little or no effect on the PVA.

One could readily theorize that the inflection point between 5 and 10% PVA for pure PVA and two PVA/ crosslinking monomer mixtures resulted from a dilute solution effect--i.e., complete separation of individual PVA molecules required intermolecular crosslinks much longer than the MBA molecules (fig. 36); however,



(non-dilute solution) (dilute solution)

(fig. 36)

simple volume calculations for individual PVA molecules (14) show this dilute solution concentration to be about 0.6% PVA. Another possibility is that the decreasing density of the chains in this region of PVA concentration noticeably decreased intermolecular forces. Less constrained individual chains could better coil onto themselves bringing their own radical into closer contact. The resulting intramolecular crosslinking between these radicals tightened individual chains, and below a critical concentration--somewhere between 5 to 10 % PVA--increased the overall

swelling capacity of the PVA gel.

The AMA seemed to scavange PVA radicals even at low PVA concentrations thus limiting overall crosslinking.

There were surprisingly few bubbles in all the samples of this series, except for those of high PVA concentration for which W(OW) and W(SW) were estimated at 0.65 gm .

V. CONCLUSIONS

1. The initial redox runs using ceric ammonium nitrate indicate that the difunctional symmetrical monomer N'-N'-methylene bis acrylamide, when reacted with equal parts of PVA produces a crosslinked PVA gel.

2. The redox system does not initiate crosslinking in a pure, low concentration (5 to 10%) PVA solution--i.e., crosslinking monomers are an essential component of this crosslinking system.

3. Two liabilities of the redox system and procedures used in this work make production of a highly crosslinked, high wt. % PVA gel virtually impossible: 1) a low weight per cent PVA solution is required to obtain mixing of the ceric and PVA solutions, and 2) the amorphous product is extremely difficult to analyze.

4. Crosslinking agents containing groups with high C_M--transfer to monomer constant--values--e.g., allylic groups--tend to inhibit crosslinking by irradiation in PVA gels. Agents with two allylic functional groups--i.e., diallylamine--completely poison crosslinking, while unsymmetrical agents with an allylic group and a reactive group--i.e., allyl acrylate and allyl methacrylate--inhibit normal PVA crosslinking to a degree.

5. N'-N'-methylene bis acrylamide produces crosslinking enhancement in irradiated 20% PVA gels. This en-

hancement is a direct function of the concentration of the crosslinking monomer in the PVA, whereas allyl acrylate and allyl methacrylate produce decreased crosslinking with increasing concentration in 20 % PVA irradiated gels.

6. N'-N'-methylene bis acrylamide produces an additive crosslinking effect to the normal crosslinking of PVA alone when added to 20% PVA and irradiated between 3 and 15 megarads. Tetra ethylene glycol dimethacrylate seems to have no effect on crosslinking while allyl acrylate and allyl methacrylate have a subtractive effect over the same dose range.

a. The effect of all four crosslinking monomers becomes insignificant at high doses--10 to 15 megarads--as increase coupling from greatly increased numbers of PVA radicals overwhelms the crosslinking effect of the monomers.

b. At low doses the crosslinking monomer effect is greatest,for the crosslinking monomer mechanisms can compete for backbone radicals with the relatively few PVA radicals.

7. N'-N'-methylene bis acrylamide increasingly enhances PVA crosslinking with increasing concentration of PVA above 20%. This is therefore a possible means of synthesizing the desired highly crosslinked, high concentration PVA material desired.

VI. RECOMMENDATIONS

1. To improve the redox system the following recommendations are made:

a. Addition of a mechanical stirrer would allow use of higher wt. % PVA solutions.

b. Higher reaction temperatures should be investigated as the viscosity would decrease, and the reaction rate would probably increase.

c. Even though the addition of the monomer in bulk non-solvated quanties resulted in non-homogenous solutions, this is the only way equal amounts of PVA and monomer can be mixed, as all the monomers the author employed were only slightly water soluble. Therefore, the bulk addition of N'-N'-methlene bis acrylamide in particular should be further investigated.

d. Other difunctional reactive monomers with low C_m values should be investigated.

2. Recommendations for improvement of the irradiation method include:

a. The use of other solvents of solvent mixtures should be investigated--1) solvent transfer effects would result, and 2) higher concentrations of organic crosslinking monomers could be attained.

b. Further efforts should be made to attain

a higher total wt. % monomer in the aqueous PVA samples--in particular, high concentrations of N'-N'-methylene bis acrylamide at low doses in high concentration PVA should be researched.

c. Monomer concentration studies of crosslinking high concentration PVA--35% and greater--with N'-N'-methylene bis acrylamide should be undertaken.

d. The crosslinking effects of other short, reactive difunctional and trifunctional monomers on irradiated PVA should be investigated. The functional groups should possess low C_M values to avoid excess homopolymerization of the monomer.

3. The effect of oxygen on irradiated PVA is at present debatable. Some correlation between oxygen content of the PVA and the properties of the resulting irradiated gel should be made.

4. Determination of the χ factor for PVA/crosslinking monomer systems would greatly aid in comparison of crosslinked gels, as the M_C value could be calculated.

5. Finally, irradiation of PVA/crosslinking monomer samples should be done under Cobalt-60 γ irradiation to investigate for low dose rate beneficial effects.

VII. CHARTS AND TABLES

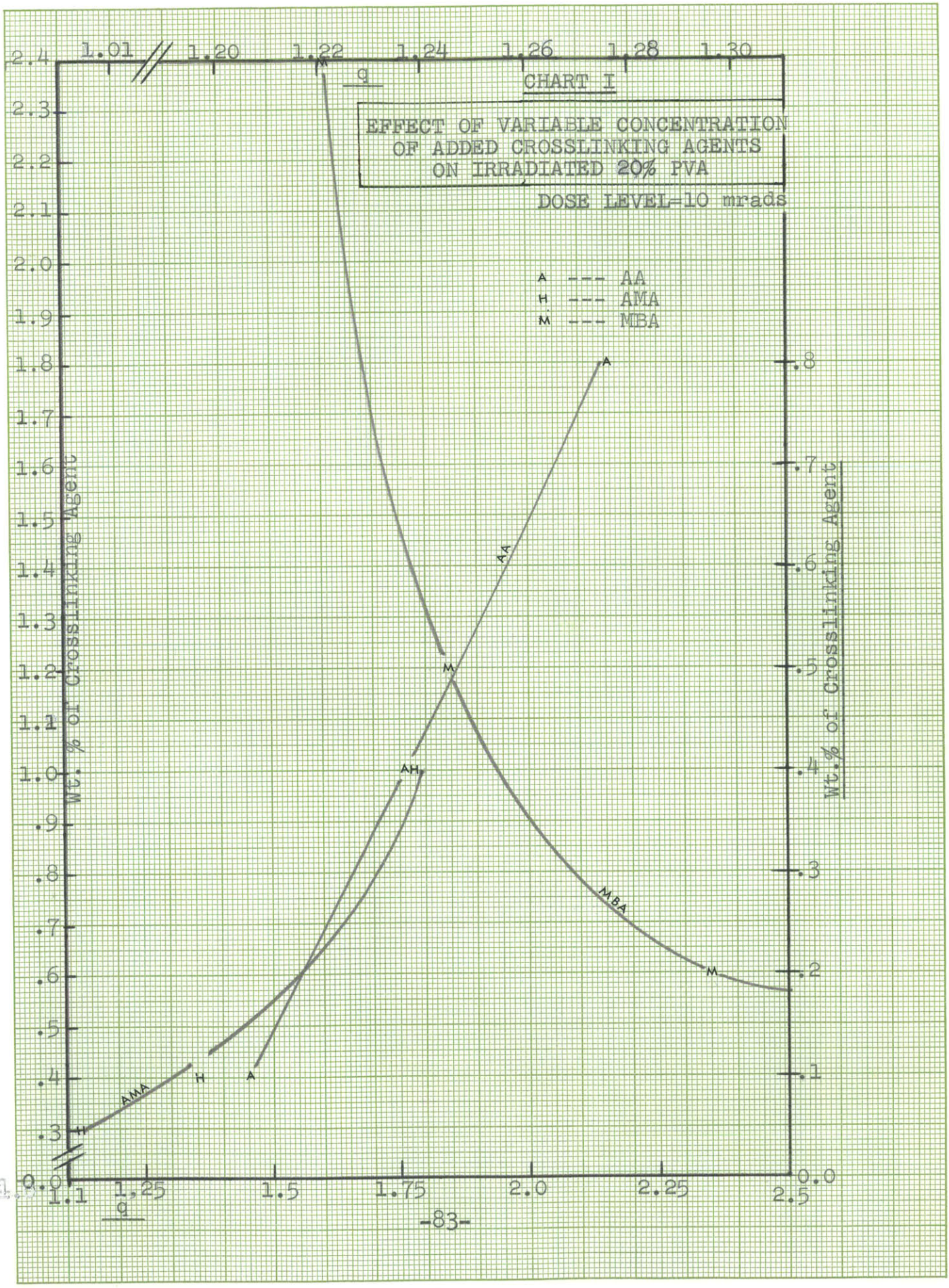
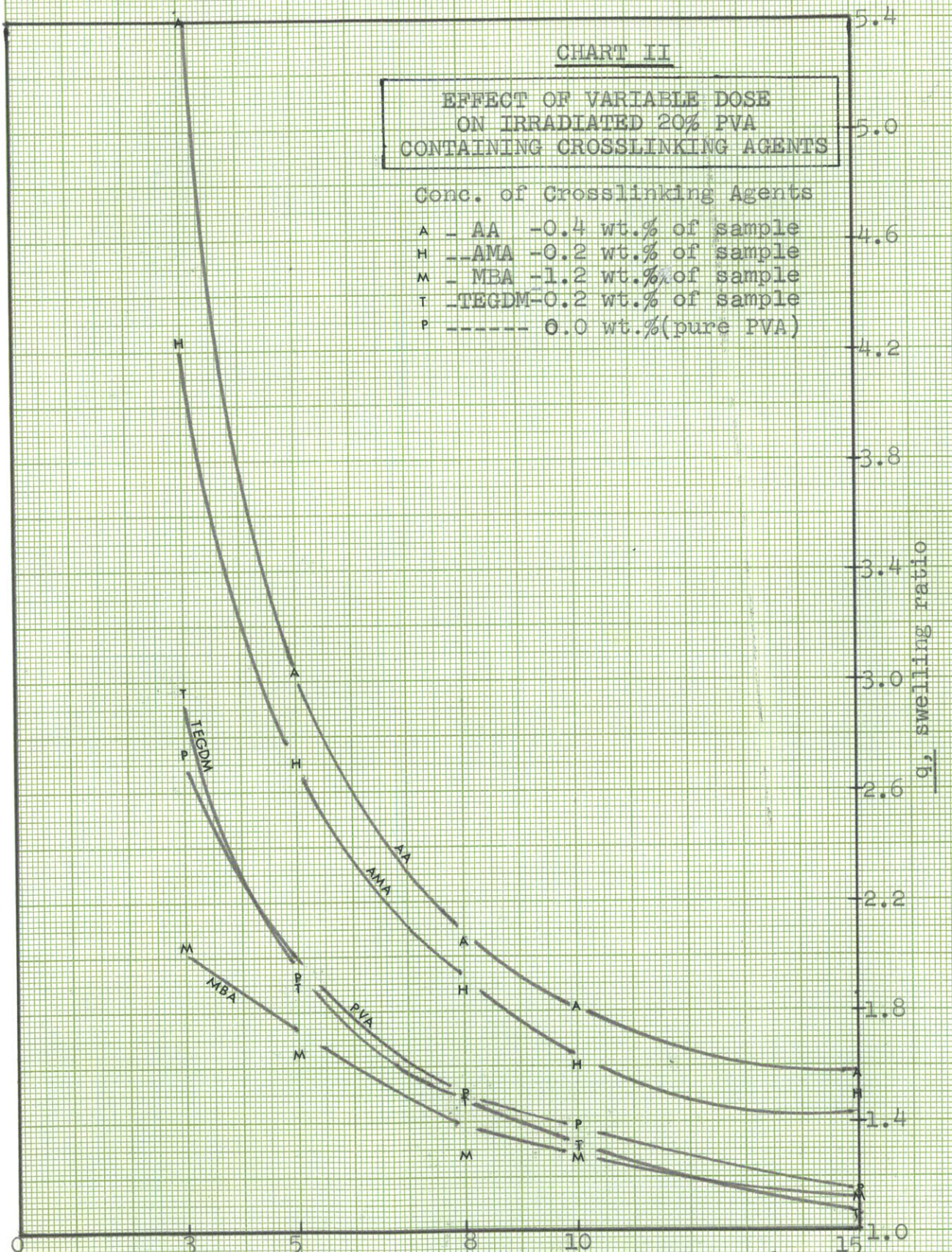


CHART II

EFFECT OF VARIABLE DOSE ON IRRADIATED 20% PVA CONTAINING CROSSLINKING AGENTS

Conc. of Crosslinking Agents

A - AA -0.4 wt.% of sample
H - AMA -0.2 wt.% of sample
M - MBA -1.2 wt.% of sample
T - TEGDM-0.2 wt.% of sample
P ------ 0.0 wt.%(pure PVA)



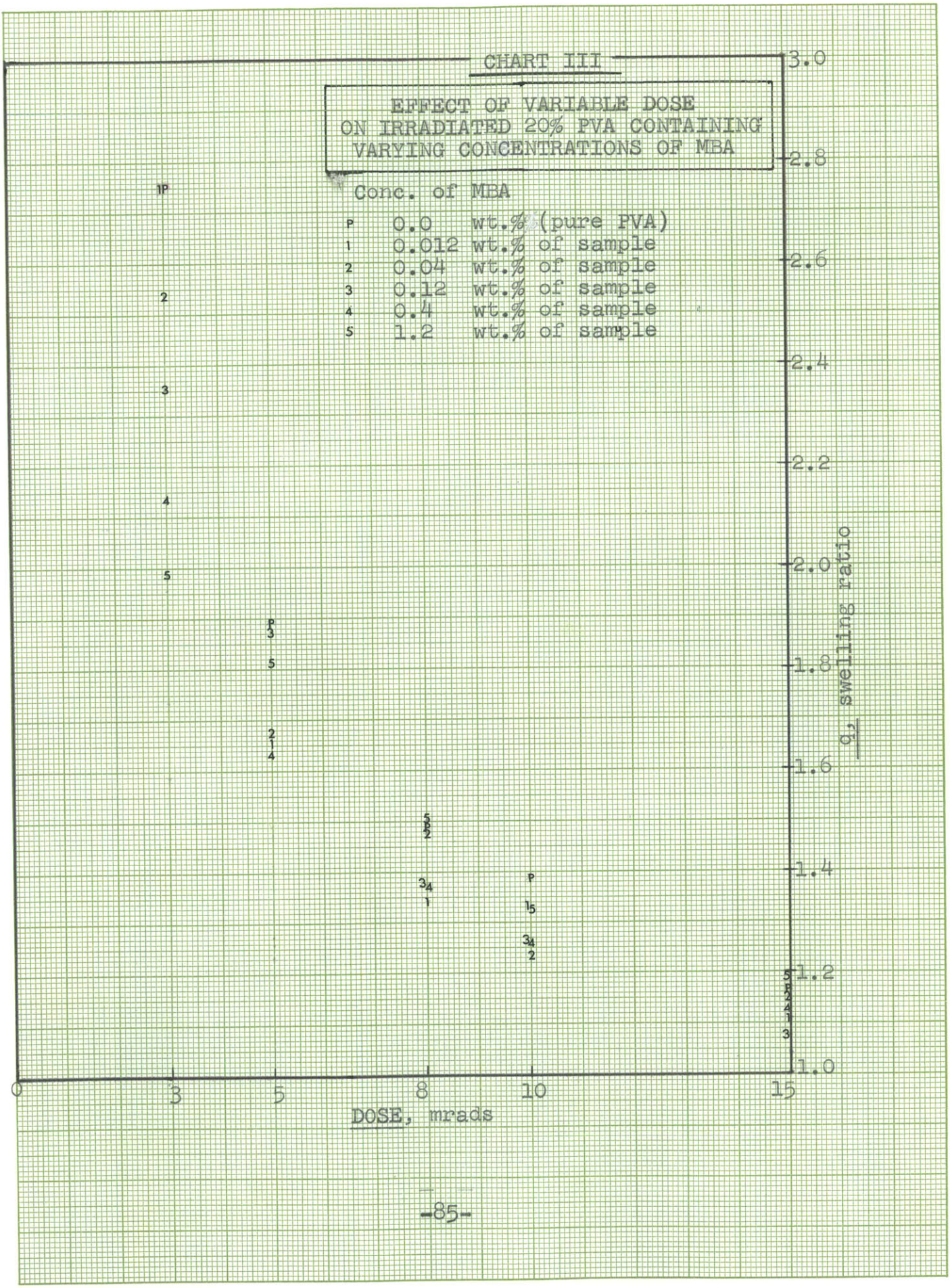


CHART III
EFFECT OF VARIABLE DOSE
ON IRRADIATED 20% PVA CONTAINING
VARYING CONCENTRATIONS OF MBA
Conc. of MBA
P 0.0 wt.% (pure PVA)
1 0.012 wt.% of sample
2 0.04 wt.% of sample
3 0.12 wt.% of sample
4 0.4 wt.% of sample
5 1.2 wt.% of sample
q, swelling ratio
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0
3
5
8
10
15
DOSE, mrads

CHART IV

EFFECT OF VARIABLE PVA CONCENTRATION ON IRRADIATED PVA CONTAINING CROSSLINKING AGENTS

DOSE LEVEL=10 mrads

Conc. of Crosslinking Agents

H -- AMA -0.35 wt.% of sample
M -- MBA -2.1 wt.% of sample
T --TEGDM-0.38 wt.% of sample
P -------- 0.0 wt.% (pure PVA)

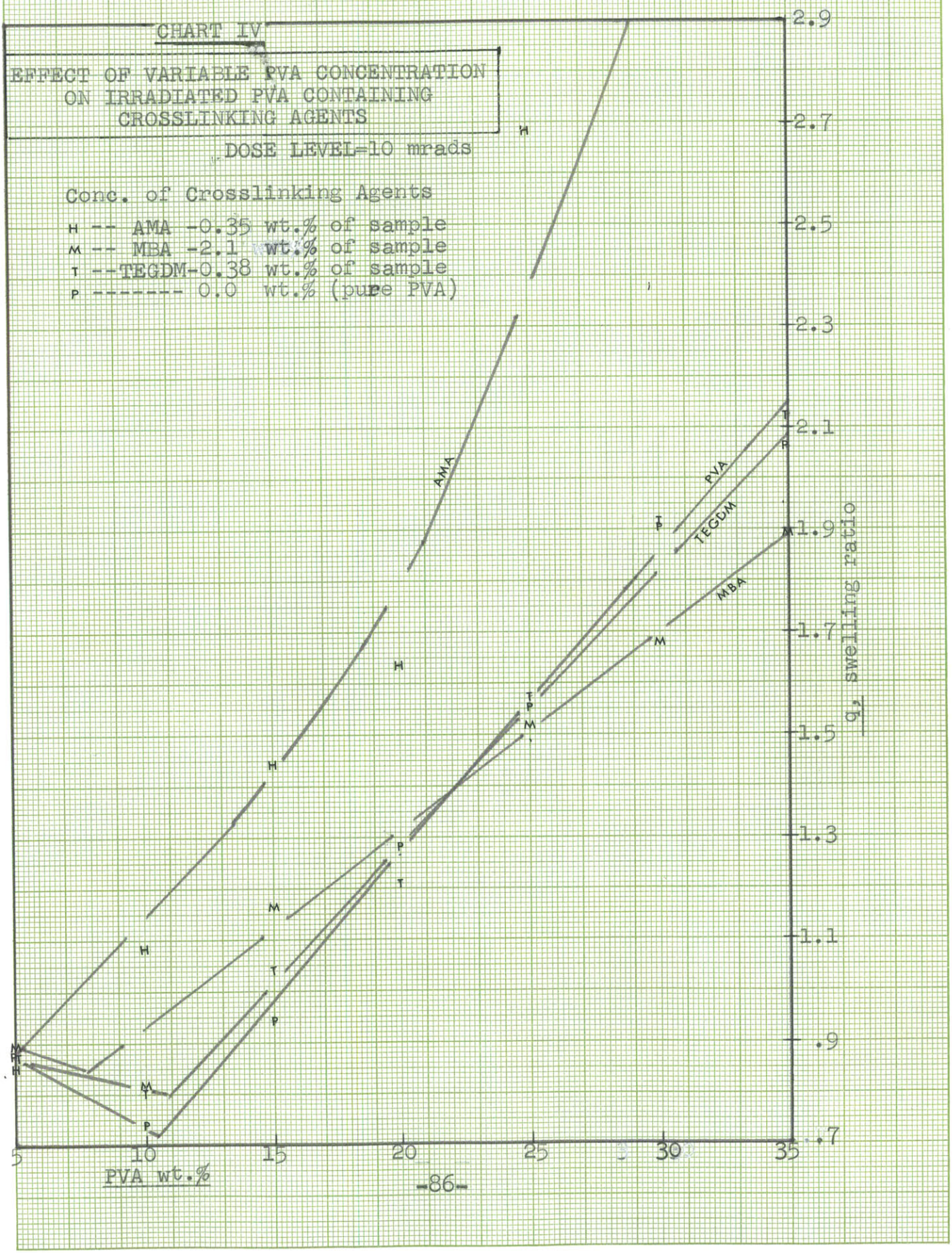


TABLE I

CROSSLINKING MONOMERS

MONOMER	MW	BACKBONE LENGTH	WATER SOLUBILITY	OTHER SOLVENTS	FUNCTIONAL GROUPS	REACTIVITY TO IRRADIATION
Allyl Acrylate	113	7	i*	ethers, alcohols	acrylic (1) allylic (1)	high
Allyl Methacrylate	126	7	i*	ethers, alcohols	acrylic (1) allylic (1)	high
Butylene Glycol Diacrylate	198	12	i		acrylic (2)	high
Diallyamine	97	7	s	ethers, alcohols	allylic (2)	
Diallyl Fumarate	196	12	i	alcohols ethers	allylic (2) vinyl (1)	low
Diethylene Glycol Diacrylate	214	13	i	ethers, alcohols	acrylic (2)	high
Ethylene Glycol Dimethacrylate	198	10	i	ethers, alcohols	acrylic (2)	
N'-N'-Methylene-bis Acrylimide	152	9	s	glycols, alcohols	acrylic (2)	
Tetra-Ethylene-Glycol Dimethacrylate	330	19	i*	alcohols ethers	acrylic (2)	high

*: a special slightly water soluble form exists

TABLE II-a

SUMMARY OF REDOX EXPERIMENTS

RUN	REACTANTS	COLOR CHANGE DURING RXN.	PRODUCT WHEN DRYED	PRODUCT SOLUBILITY AT 90 °C	YIELD (% GRAFT)
1	100 gm 10% PVA 25 ml .1M Ceric (.0218 moles/l)	Dull red to Clear	Brittle, yellow, crystalline	s	
2	90 gm 10% PVA 10 ml TEGDM 25 ml .1 M Ceric (.0236 moles/l)	Dull red to Clear	white clumps; cottage cheese appearance		12 gm (30%)
3	100 gm 10% PVA 10 gm MBA 25 ml .1 M Ceric (.0218 moles/l)	Dull red to Clear	Opaque; brittle; crystalline		20 gm (100%)
4	80 gm 10% PVA 8 gm MBA 20 ml .1 M Ceric (.0219 moles/l)	Dull red to Clear	Opaque; brittle crystalline	s	17 gm (100 %)
5	80 gm 10% PVA 2 gm MBA 20 ml .1 M Ceric (.0219 moles/l)	Dull red to Clear	Not Dryed	i	

TABLE II-b

SUMMARY OF REDOX EXPERIMENTS

RUN	REACTANTS	COLOR CHANGE DURING RXN.	PRODUCT WHEN DRYED	PRODUCT SOLUBILITY AT 90 °C	YIELD (% GRAFT)
6	78 gm 5.4% PVA 10 ml .1 M Ceric (.0119 moles/l)	Dull Red to Clear	Not Dryed	s	
7 a	40 gm 9% PVA	Both runs abandoned prior to addition of Ceric--too viscous			
b	40 gm 13% PVA				
8 a	40.1 gm 5% PVA 5.01 ml .01 M Ceric (.00116 moles/l)	Yellow to Clear	Not Dryed	s	
b	44.2 gm 5% PVA 5.5 ml 1.0 M Ceric (.116 moles/l)	Black to Brown	Not Dryed	s	
9 a	33 gm 5% PVA 5 ml 3% MBA 4.12 ml .1 M Ceric (.0102 moles/l)	Dull red to Clear	Not Dryed	i	
b	27 gm 5% PVA 10 ml .5% TEGDM 3.38 ml .1 M Ceric (.00865 moles/l)	Dull red to Clear	Not Dryed	s	

TABLE II-c

SUMMARY OF REDOX EXPERIMENTS

RUN	REACTANTS	COLOR CHANGE DURING RXN.	PRODUCT	PRODUCT SOLUBILITY AT 90 °C	YIELD (% GRAFT)
9 c	31 gm 5% PVA 5 ml .5% TEGDM 3.88 ml .1 M Ceric (.0101 moles/10	Dull red to Clear		s	
10 a	62 gm 15% PVA 16.3 ml 3% MBA 23.25 ml .1 M Ceric (.0255 moles/1)	Dull red to Clear		i	
b	42 gm 15% PVA 8.3 ml 5% DAA 15.75 ml .1 M Ceric	Dull red to Clear		s	
c	31 gm 15% PVA 24.5 ml .1% AA 11.62 ml .1 M Ceric (.0186 moles/1)	Dull red to Clear		s	

TABLE III

VARIABLES OF THE FOUR IRRADIATION SERIES

SERIES	TOTAL DOSE (dose, mrads)	C.L. MONOMER CONC. (monomers)	PVA CONC. (wt.%)
A	Const. (10)	Variable (AA,AMA,DAA,MBA,TEGDM)	Const. (20)
B	Variable (3,5,8,10,15)	Const. (AA,AMA,DAA,MBA,TEGDM)	Const. (20)
C	Variable (3,5,8,10,15)	Variable (MBA)	Const. (20)
D	Const. (10)	Const. (AMA,MBA,TEGDM)	Variable (5-35)

TABLE IV

DENSITY DETERMINATION OF THE PURE CROSSLINKING MONOMERS

C.L. AGENT	VOLUME (cc)	WEIGHT (gm)	DENSITY (gm/cc)
AA	50	47.077	0.942
AMA	50	46.9347	0.934
MBA	25	25.02	1.0
DAA	50	39.1542	0.783

TABLE V-a

A SERIES--IRRADIATION

NO.	PVA (gm)	SOLV. (ml)	CROSSLINKING AGENT	(ml)	Conc. (%)	COMPOSITION PVA (wt.%)	C.L. (wt.%)	DOSE Total (mrads)	Hist. (mrads)	OBSERVATIONS AFTER IRRADIATION
A-01	2.000	8.00	AA	.085	100.	20.0	0.8	10	5,5	bubbles;tacky
A-02	2.000	8.00	AA	.042	100.	20.0	0.4	10	5,5	bubbles;tacky
A-03	2.000	8.00	AA	.011	100.	20.0	0.1	10	5,5	bubbles;tacky
A-04	2.000	8.00	AMA	.043	100.	20.0	0.4	10	5,5	bubbles;tacky
A-05	2.000	8.00	AMA	.011	100.	20.0	0.1	10	5,5	bubbles;tacky
A-06	2.000	8.00	AMA	.0054	100.	20.0	0.05	10	5,5	bubbles;tacky
A-07	2.000	8.00	DAA	.409	100.	20.0	3.2	10	5,5	few bubbles; very tacky
A-08	2.000	8.00	DAA	.128	100.	20.0	1.0	10	5,5	few bubbles; very tacky
A-09	2.000	8.00	DAA	.064	100.	20.0	0.5	10	5,5	few bubbles; very tacky
A-10	2.000	8.00	MBA	.24	100.	20.0	2.4	10	5,5	bubbles;low tackiness;cloudy
A-11	2.000	8.00	MBA	.12	100.	20.0	1.2	10	5,5	bubbles;low tackiness;cloudy
A-12	2.000	8.00	MBA	.06	100.	20.0	0.6	10	5,5	bubbles;low tackiness;cloudy

TABLE V-b

A SERIES--IRRADIATION

NO.	PVA (gm)	SOLV. (ml)	CROSSLINKING AGENT	(ml)	Conc. (%)	COMPOSITION PVA (wt.%)	C.L. (wt.%)	DOSE Total (mrads)	Hist. (mrads)	OBSERVATIONS AFTER IRRADIATION
A-13	2.000	8.00	AA	.085	100.	20.0	0.8	10	5,5	bubbles;tacky
A-14	2.000	8.00	AMA	.043	100.	20.0	0.4	10	5,5	bubbles;tacky
A-15	2.000	8.00	MBA	.24	100.	20.0	2.4	10	5,5	bubbles;low tackiness;cloudy
A-16	2.000	8.00	DAA	.409	100.	20.0	3.2	10	5,5	few bubbles; very tacky
A-17	2.000	8.00	---	----	----	20.0	0.0	10	5,5	bubbles;tacky
A-18	2.000	8.00	---	----	----	20.0	0.0	10	5,5	bubbles;tacky

TABLE VI-a

A SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	W(OA) (gm)	W(OW) (gm)	W(SA) (gm)	W(SW) (gm)	OBSERVATIONS AFTER SWELLING	W(D) (gm)
A-01	AA	20.0	0.8	9.2284	----	18.9833	.3969	no bubbles	1.8809
A-02	AA	20.0	0.4	9.6126	----	16.5145	.3719	no bubbles	1.9028
A-03	AA	20.0	0.1	9.1334	.0685	12.6680	.4209	no bubbles	2.0037
A-04	AMA	20.0	0.4	9.6436	----	16.7679	.4183	no bubbles	1.9341
A-05	AMA	20.0	0.1	9.4922	.1644	12.7222	.4420	no bubbles	2.0281
A-06	AMA	20.0	0.05	10.9788	.2948	12.1679	.4411	no bubbles	2.0351
A-07	DAA	20.0	3.2	7.9004	----	---	---	dissolved	---
A-08	DAA	20.0	1.0	8.8606	.3900	---	---	dissolved	---
A-09	DAA	20.0	0.5	8.6426	.0460	26.9519	.3867	no bubbles	1.7200
A-10	MBA	20.0	2.4	9.4342	.2469	11.4975	.5026	no bubbles	2.3455
A-11	MBA	20.0	1.2	9.1302	.3203	11.3373	.5046	no bubbles	2.1500
A-12	MBA	20.0	0.6	9.0334	.2746	11.6351	.5046	no bubbles	2.0910

TABLE VI-b

A SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	W(OA) (gm)	W(OW) (gm)	W(SA) (gm)	W(SW) (gm)	OBSERVATIONS AFTER SWELLING	W(D) (gm)
A-13	AA	20.0	0.8	9.2929	.0263	18.9900	.3747	no bubbles	1.8955
A-14	AMA	20.0	0.4	9,5281	---	16.9135	.4083	no bubbles	1.9596
A-15	MBA	20.0	2.4	9.1400	.2376	11.5041	.5251	no bubbles	2.3578
A-16	DAA	20.0	3.2	7.5212	.4012	---	---	dissolved	---
A-17	---	20.0	0.0	9.1550	.1789	11.3840	.4668	no bubbles	1.9338
A-18	---	20.0	0.0	9.3368	.2232	11.9041	.4518	no bubbles	2.0557

TABLE VII-a

A SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	V(P) (cc)	V(R) (cc)	V(S) (cc)	v(R)	v(S)	v(2m)	q
A-01	AA	20.0	0.8	1.482	8.82	18.661	.168	.0794	.4726	2.116
A-02	AA	20.0	0.4	1.499	9.21	16.207	.163	.0925	,5682	1.760
A-03	AA	20.0	0.1	1.579	8.73	12.296	.181	.1284	.7100	1.408
A-04	AMA	20.0	0.4	1.524	9.24	16.415	.165	.0928	.5629	1.776
A-05	AMA	20.0	0.1	1.598	9.09	12.330	.176	.1296	.7372	1.356
A-06	AMA	20.0	0.05	1.604	10.57	11.774	.152	.1362	.8977	1.114
A-07	DAA	20.0	3.2	---	7.50	---	--	---	---	---
A-08	DAA	20.0	1.0	---	8.82	---	--	---	---	---
A-09	DAA	20.0	0.5	1.355	8.24	26.672	.164	.0508	.3089	3.237
A-10	MBA	20.0	2.4	1.848	9.03	11.039	.204	.1674	.8180	1.222
A-11	MBA	20.0	1.2	1.694	8.73	10.876	.194	.1558	.8302	1.245
A-12	MBA	20.0	0.6	1.648	8.63	11.175	.191	.1475	.7722	1.295

TABLE VII-b

A SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	V(P) (cc)	V(R) (cc)	V(S) (cc)	v(R)	v(S)	v(2m)	q
A-13	AA	20.0	0.8	1.494	8.89	16.690	.168	.0895	.4756	2.102
A-14	AMA	20.0	0.4	1.544	9.12	16.571	.169	.0932	.5503	1.817
A-15	MBA	20.0	2.4	1.858	8.74	10.833	.212	.1715	.7929	1.261
A-16	DAA	20.0	3.2	---	7.12	---	--	---	---	---
A-17	---	20.0	0.0	1.524	8.75	10.961	.174	.1390	.7983	1.253
A-18	---	20.0	0.0	1.620	8.93	11.498	.181	.1409	.7792	1.283

TABLE VIII-a

B SERIES--IRRADIATION

NO.	PVA (gm)	SOLV. (ml)	CROSSLINKING AGENT	(ml)	Conc. (%)	COMPOSITION PVA (wt.%)	C.L. (wt.%)	DOSE Total (mrads)	Hist. (mrads)	OBSERVATIONS AFTER IRRADIATION
B-01	2.000	8.00	AA	4.00	1.0	20.0	0.4	3	3	no bubbles; very tacky
B-02	2.000	8.00	AA	4.00	1.0	20.0	0.4	5	5	few bubbles; tacky
B-03	2.000	8.00	AA	4.00	1.0	20.0	0.4	8	5,3	some bubbles; low tackiness
B-04	2.000	8.00	AA	4.00	1.0	20.0	0.4	10	5,5	bubbles;not tacky
B-05	2.000	8.00	AA	4.00	1.0	20.0	0.4	15	5,5,5	many bubbles; not tacky
B-06	2.000	8.00	AMA	4.00	0.5	20.0	0.2	3	3	no bubbles; very tacky
B-07	2.000	8.00	AMA	4.00	0.5	20.0	0.2	5	5	few bubbles; tacky
B-08	2.000	8.00	AMA	4.00	0.5	20.0	0.2	8	5,3	some bubbles; low tackiness
B-09	2.000	8.00	AMA	4.00	0.5	20.0	0.2	10	5,5	bubbles;not tacky
B-10	2.000	8.00	AMA	4.00	0.5	20.0	0.2	15	5,5,5	many bubbles; not tacky
B-11	2.000	8.00	MBA	4.00	3.0	20.0	1.2	3	3	no bubbles; low tackiness
B-12	2.000	8.00	MBA	4.00	3.0	20.0	1.2	5	5	few bubbles; not tacky

TABLE VIII-b

B SERIES--IRRADIATION

NO.	PVA (gm)	SOLV. (ml)	CROSSLINKING AGENT	(ml)	Conc. (%)	COMPOSITION PVA (wt.%)	C.L. (wt.%)	DOSE Total (mrads)	Hist. (mrads)	OBSERVATIONS AFTER IRRADIATION
B-13	2.000	8.00	MBA	4.00	3.0	20.0	1.2	8	5,3	some bubbles; not tacky
B-14	2.000	8.00	MBA	4.00	3.0	20.0	1.2	10	5,5	bubbles;not tacky
B-15	2.000	8.00	MBA	4.00	3.0	20.0	1.2	15	5,5,5	many bubbles; not tacky
B-16	2.000	8.00	DAA	4.00	4.0	20.0	1.6	3	3	no bubbles very tacky
B-17	2.000	8.00	DAA	4.00	4.0	20.0	1.6	5	5	few bubbles very tacky
B-18	2.000	8.00	DAA	4.00	4.0	20.0	1.6	8	5,3	some bubbles; tacky
B-19	2.000	8.00	DAA	4.00	4.0	20.0	1.6	10	5,5	bubbles;tacky
B-20	2.000	8.00	DAA	4.00	4.0	20.0	1.6	15	5,5,5	many bubbles; low tackiness
B-21	2.000	8.00	TEGDM	4.00	0.54	20.0	0.22	3	3	no bubbles; not tacky
B-22	2.000	8.00	TEGDM	4.00	0.54	20.0	0.22	5	5	no bubbles; not tacky
B-23	2.000	8.00	TEGDM	4.00	0.54	20.0	0.22	8	5,3	no bubbles; not tacky
B-24	2.000	8.00	TEGDM	4.00	0.54	20.0	0.22	10	5,5	no bubbles; not tacky
B-25	2.000	8.00	TEGDM	4.00	0.54	20.0	0.22	15	5,5,5	few bubbles; not tacky

TABLE IX-a

B SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	W(OA) (gm)	W(OW) (gm)	W(SA) (gm)	W(SW) (gm)	OBSERVATIONS AFTER SWELLING	W(D) (gm)
B-01	AA	20.0	0.4	8.2370	---	42.9569	.3682	no bubbles	1.4538
B-02	AA	20.0	0.4	7.8024	---	22.6875	.3976	no bubbles	1.6526
B-03	AA	20.0	0.4	8,1924	---	16.4144	.4415	no bubbles	1.8762
B-04	AA	20.0	0.4	8.2173	---	14.5321	.4441	no bubbles	1.9356
B-05	AA	20.0	0.4	8.0447	---	12.3515	.4269	no bubbles	1.8714
B-06	AMA	20.0	0.2	8.4302	---	34.2962	.3647	no bubbles	1.5202
B-07	AMA	20.0	0.2	8.4525	---	22.0736	.4108	no bubbles	1.7545
B-08	AMA	20.0	0.2	8.1924	---	15.0480	.4467	no bubbles	1.9030
B-09	AMA	20.0	0.2	8.6018	---	13.6019	.4430	no bubbles	1.9512
B-10	AMA	20.0	0.2	7.9852	---	11.8270	.4412	no bubbles	1.9256
B-11	MBA	20.0	1.2	9.5134	---	19.0032	.4752	no bubbles	1.9856
B-12	MBA	20.0	1.2	9.2634	---	15.0627	.4812	no bubbles	2.0560

TABLE IX-b

B SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	W(OA) (gm)	W(OW) (gm)	W(SA) (gm)	W(SW) (gm)	OBSERVATIONS AFTER SWELLING	W(D) (gm)
B-13	MBA	20.0	1.2	9.6572	---	12.2834	.4754	no bubbles	2.1386
B-14	MBA	20.0	1.2	9.1375	---	11.4151	.4635	no bubbles	2.0900
B-15	MBA	20.0	1.2	9.1730	---	10.5338	.4720	no bubbles	2.0755
B-16	DAA	20.0	1.6	9.0474	---	---	----	dissolved	---
B-17	DAA	20.0	1.6	9.0288	---	---	----	dissolved	---
B-18	DAA	20.0	1.6	9.1791	---	---	----	dissolved	---
B-19	DAA	20.0	1.6	9.3959	---	---	----	dissolved	---
B-20	DAA	20.0	1.6	9.1407	---	---	----	dissolved	---
B-21	TEGDM	20.0	0.3	9.2035	.3862	27.5419	.3735	no bubbles	1.6350
B-22	TEGDM	20.0	0.3	9.6428	.4123	19.1347	.4405	no bubbles	2.1960
B-23	TEGDM	20.0	0.3	9.4230	.4035	14.8221	.4515	no bubbles	1.9876
B-24	TEGDM	20.0	0.3	9.7719	.4230	13.7351	.4757	no bubbles	2.0403
B-25	TEGDM	20.0	0.3	9.2785	.3612	10.7655	.4220	no bubbles	2.0028

TABLE X-a

B SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	V(P) (cc)	V(R) (cc)	V(S) (cc)	v(R)	v(S)	v(2m)	q
B-01	AA	20.0	0.4	1.146	7.84	42.760	.146	.0270	.1833	5.454
B-02	AA	20.0	0.4	1.302	7.40	22.380	.176	.0586	.3307	3.024
B-03	AA	20.0	0.4	1.478	7.79	16.037	.190	.0929	.4858	2.059
B-04	AA	20.0	0.4	1.525	7.82	14.144	.195	.1087	.5529	1.809
B-05	AA	20.0	0.4	1.475	7.64	11.972	.193	.1241	.6381	1.567
B-06	AMA	20.0	0.2	1.198	8.03	34.068	.149	.0354	.2357	4.242
B-07	AMA	20.0	0.2	1.382	8.05	21.750	.172	.0641	.3701	2.702
B-08	AMA	20.0	0.2	1.500	7.79	14.660	.192	.1031	.5314	1.882
B-09	AMA	20.0	0.2	1.538	8.20	13.212	.188	.1173	.6206	1.611
B-10	AMA	20.0	0.2	1.517	7.58	11.431	.200	.1338	.6631	1.508
B-11	MBA	20.0	1.2	1.565	9.11	18.602	.172	.0848	.4897	2.042
B-12	MBA	20.0	1.2	1.620	8.86	14.640	.183	.1156	.6052	1.652

TABLE X-b

B SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	V(P) (cc)	V(R) (cc)	V(S) (cc)	v(R)	v(S)	v(2m)	q
B-13	MBA	20.0	1.2	1.685	9.25	11.855	.182	.1433	.7802	1.282
B-14	MBA	20.0	1.2	1.647	8.73	10.996	.189	.1510	.7940	1.260
B-15	MBA	20.0	1.2	1.636	8.77	10.102	.186	.1632	.8681	1.152
B-16	DAA	20.0	1.6	---	--	---	--	---	---	---
B-17	DAA	20.0	1.6	---	--	---	--	---	---	---
B-18	DAA	20.0	1.6	---	--	---	--	---	---	---
B-19	DAA	20.0	1.6	---	--	---	--	---	---	---
B-20	DAA	20.0	1.6	---	--	---	--	---	---	---
B-21	TEGDM	20.0	0.3	1.288	8.835	26.268	.146	.0490	.336	2.973
B-22	TEGDM	20.0	0.3	1.730	9.249	17.760	.187	.0974	.521	1.920
B-23	TEGDM	20.0	0.3	1.566	9.038	13.419	.173	.117	.673	1.485
B-24	TEGDM	20.0	0.3	1.608	9.368	12.304	.172	.131	.761	1.313
B-25	TEGDM	20.0	0.3	1.578	8.935	9.376	.177	.168	.953	1.049

TABLE XI-a

C SERIES--IRRADIATION

NO.	PVA (gm)	SOLV. (ml)	CROSSLINKING AGENT	(ml)	Conc. (%)	COMPOSITION PVA (wt.%)	C.L. (wt.%)	DOSE Total (mrads)	Hist. (mrads)	OBSERVATIONS AFTER IRRADIATION
C-01	2.000	8.00	MBA	4.00	0.03	20.0	0.012	3	3	no bubbles; tacky
C-02	2.000	8.00	MBA	4.00	0.03	20.0	0.012	5	5	few bubbles; tacky
C-03	2.000	8.00	MBA	4.00	0.03	20.0	0.012	8	5,3	some bubbles; low tackiness
C-04	2.000	8.00	MBA	4.00	0.03	20.0	0.012	10	5,5	bubbles;not tacky
C-05	2.000	8.00	MBA	4.00	0.03	20.0	0.012	15	5,5,5	many bubbles; not tacky
C-06	2.000	8.00	MBA	4.00	0.10	20.0	0.04	3	3	no bubbles; low tackiness
C-07	2.000	8.00	MBA	4.00	0.10	20.0	0.04	5	5	few bubbles; low tackiness
C-08	2.000	8.00	MBA	4.00	0.10	20.0	0.04	8	5,3	some bubbles; not tacky
C-09	2.000	8.00	MBA	4.00	0.10	20.0	0.04	10	5,5	bubbles;not tacky
C-10	2.000	8.00	MBA	4.00	0.10	20.0	0.04	15	5,5,5	many bubbles; not tacky
C-11	2.000	8.00	MBA	4.00	0.3	20.0	0.12	3	3	no bubbles; low tackiness
C-12	2.000	8.00	MBA	4.00	0.3	20.0	0.12	5	5	few bubbles; not tacky

TABLE XI-b

C SERIES--IRRADIATION

NO.	PVA (gm)	SOLV. (ml)	CROSSLINKING AGENT	(ml)	Conc. (%)	COMPOSITION PVA (wt.%)	C.L. (wt.%)	DOSE Total (mrads)	Hist. (mrads)	OBSERVATIONS AFTER IRRADIATION
C-13	2.000	8.00	MBA	4.00	0.3	20.0	0.12	8	5,3	some bubbles; not tacky
C-14	2.000	8.00	MBA	4.00	0.3	20.0	0.12	10	5,5	bubbles;not tacky
C-15	2.000	8.00	MBA	4.00	0.3	20.0	0.12	15	5,5,5	many bubbles; not tacky
C-16	2.000	8.00	MBA	4.00	1.0	20.0	0.4	3	3	no bubbles low tackiness
C-17	2.000	8.00	MBA	4.00	1.0	20.0	0.4	5	5	few bubbles; not tacky
C-18	2.000	8.00	MBA	4.00	1.0	20.0	0.4	8	5,3	some bubbles not tacky
C-19	2.000	8.00	MBA	4.00	1.0	20.0	0.4	10	5,5	bubbles;not tacky
C-20	2.000	8.00	MBA	4.00	1.0	20.0	0.4	15	5,5,5	many bubbles; not tacky
C-21	2.000	8.00	MBA	4.00	3.0	20.0	1.2	3	3	no bubbles; low tackiness
C-22	2.000	8.00	MBA	4.00	3.0	20.0	1.2	5	5	few bubbles; not tacky
C-23	2.000	8.00	MBA	4.00	3.0	20.0	1.2	8	5,3	some bubbles; not tacky
C-24	2.000	8.00	MBA	4.00	3.0	20.0	1.2	10	5,5	bubbles;not tacky
C-25	2.000	8.00	MBA	4.00	3.0	20.0	1.2	15	5,5,5	many bubbles; not tacky

TABLE XII-a

C SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	W(OA) (gm)	W(OW) (gm)	W(SA) (gm)	W(SW) (gm)	OBSERVATIONS AFTER SWELLING	W(D) (gm)
C-01	MBA	20.0	0.012	8.7075	---	23.2400	.4073	no bubbles	1.7751
C-02	MBA	20.0	0.012	9.3988	---	15.3336	.4319	no bubbles	1.9151
C-03	MBA	20.0	0.012	9.5381	---	12.6340	.1698	many bubbles	2.0292
C-04	MBA	20.0	0.012	8.4985	---	11.1351	.3832	few bubbles	2.0407
C-05	MBA	20.0	0.012	8.9836	---	9.9102	---	many bubbles	1.9687
C-06	MBA	20.0	0.04	8.4353	---	20.7680	.3715	no bubbles	1.8416
C-07	MBA	20.0	0.04	9.3523	---	15.3461	.4081	no bubbles	2.0362
C-08	MBA	20.0	0.04	8.7704	---	12.7312	.2017	few bubbles	2.0209
C-09	MBA	20.0	0.04	9.2979	---	11.3530	---	many bubbles	2.0514
C-10	MBA	20.0	0.04	8.8939	---	10.1975	---	many bubbles	2.0268
C-11	MBA	20.0	0.12	9.2758	---	21.2424	.3732	no bubbles	1.8100
C-12	MBA	20.0	0.12	8.6522	---	15.8182	.3900	no bubbles	1.9133

TABLE XII-b

C SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	W(OA) (gm)	W(OW) (gm)	W(SA) (gm)	W(SW) (gm)	OBSERVATIONS AFTER SWELLING	W(D) (gm)
C-13	MBA	20.0	0.12	9.3980	---	12.7712	.1794	bubbles	1.9903
C-14	MBA	20.0	0.12	9.2582	---	11.5513	.0999	bubbles	2.0049
C-15	MBA	20.0	0.12	8.7422	---	9.3586	---	many bubbles	1.9860
C-16	MBA	20.0	0.4	9.3714	---	19.5745	.4293	no bubbles	1.8458
C-17	MBA	20.0	0.4	9.2545	---	14.8417	.4315	no bubbles	1.9763
C-18	MBA	20.0	0.4	9.2152	---	12.5242	.2792	bubbles	2.0919
C-19	MBA	20.0	0.4	9.1854	---	11.5009	.0938	bubbles	2.0159
C-20	MBA	20.0	0.4	8.8818	---	9.9882	---	many bubbles	2.0001
C-21	MBA	20.0	1.2	8.7928	---	17.1146	.4564	no bubbles	2.0147
C-22	MBA	20.0	1.2	6.8724	---	12.1357	.4386	no bubbles	1.9842
C-23	MBA	20.0	1.2	7.4418	---	10.9675	.4143	no bubbles	2.0423
C-24	MBA	20.0	1.2	8.4875	---	11.1421	.2373	bubbles	2.0927
C-25	MBA	20.0	1.2	8.4284	---	10.0173	---	many bubbles	2.1029

TABLE XIII-a

C SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	V(P) (cc)	V(R) (cc)	V(S) (cc)	v(R)	v(S)	v(2m)	q
C-01	MBA	20.0	0.012	1.399	8.324	22.924	.168	.0610	.363	2.754
C-02	MBA	20.0	0.012	1.509	9.017	14.961	.167	.101	.603	1.659
C-03	MBA	20.0	0.012	1.599	9.156	12.283	.174	.130	.745	1.341
C-04	MBA	20.0	0.012	1.608	8.115	10.795	.198	.149	.752	1.330
C-05	MBA	20.0	0.012	1.551	8.601	9.548	.180	.163	.901	1.110
C-06	MBA	20.0	0.04	1.452	8.051	20.478	.180	.0709	.394	2.538
C-07	MBA	20.0	0.04	1.605	8.970	14.998	.179	.107	.598	1.672
C-08	MBA	20.0	0.04	1.592	8.357	12.380	.190	.129	.677	1.476
C-09	MBA	20.0	0.04	1.616	8.916	10.997	.181	.147	.811	1.233
C-10	MBA	20.0	0.04	1.597	8.511	9.837	.188	.1162	.865	1.156
C-11	MBA	20.0	0.12	1.426	8.893	7.820	.160	.0681	.424	2.356
C-12	MBA	20.0	0.12	1.508	8.269	15.490	.182	.0973	.534	1.873

TABLE XIII-b

C SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	V(P) (cc)	V(R) (cc)	V(S) (cc)	v(R)	v(S)	v(2m)	q
C-13	MBA	20.0	0.12	1.568	9.016	12.421	.174	.126	.726	1.378
C-14	MBA	20.0	0.12	1.580	8.876	11.196	.178	.141	.793	1.261
C-15	MBA	20.0	0.12	1.565	8.359	8.994	.187	.174	.929	1.076
C-16	MBA	20.0	0.4	1.454	8.989	19.222	.162	.0757	.468	2.138
C-17	MBA	20.0	0.4	1.557	8.872	14.468	.176	.108	.613	1.631
C-18	MBA	20.0	0.4	1.648	8.833	12.173	.187	.135	.726	1.378
C-19	MBA	20.0	0.4	1.588	8.803	11.145	.180	.142	.790	1.266
C-20	MBA	20.0	0.4	1.576	8.499	9.627	.185	.164	.883	1.133
C-21	MBA	20.0	1.2	1.588	8.410	16.725	.189	.0949	.503	1.989
C-22	MBA	20.0	1.2	1.564	6.485	11.744	.241	.133	.552	1.811
C-23	MBA	20.0	1.2	1.609	7.056	10.596	.228	.152	.666	1.502
C-24	MBA	20.0	1.2	1.649	8.104	10.785	.203	.153	.751	1.331
C-25	MBA	20.0	1.2	1.657	8.044	9.656	.206	.172	.833	1.200

TABLE XIV-a

D SERIES--IRRADIATION

NO.	PVA (gm)	SOLV. (ml)	CROSSLINKING AGENT	(ml)	Conc. (%)	COMPOSITION PVA (wt.%)	C.L. (wt.%)	DOSE Total (mrads)	Hist. (mrads)	OBSERVATIONS AFTER IRRADIATION
D-01	3.000	5.50	MBA	5.50	3.0	35.3	1.75	10	5,5	many bubbles; not tacky
D-02	3.000	7.00	MBA	7.00	3.0	30.0	2.1	10	5,5	bubbles;not tacky
D-03	3.000	9.00	MBA	8.40	3.0	25.0	2.1	10	5,5	few bubbles; not tacky
D-04	2.000	8.00	MBA	7.00	3.0	20.0	2.1	10	5,5	few bubbles; not tacky
D-05	2.000	8.00	MBA	9.31	3.0	15.0	2.1	10	5,5	few bubbles; not tacky
D-06	1.000	8.00	MBA	7.00	3.0	10.0	2.1	10	5,5	no bubbles; not tacky
D-07	0.500	8.00	MBA	7.00	3.0	5.0	2.1	10	5,5	shrank from sides;opaque
D-08	3.000	8.00	AMA	5.50	0.5	35.3	0.275	10	5,5	many bubbles; not tacky
D-09	3.000	8.00	AMA	7.00	0.5	30.0	0.35	10	5,5	many bubbles; not tacky
D-10	3.000	8.00	AMA	8.40	0.5	25.0	0.35	10	5,5	some bubbles; not tacky
D-11	2.000	8.00	AMA	7.00	0.5	20.0	0.35	10	5,5	some bubbles; not tacky
D-12	1.000	8.00	AMA	9.31	0.5	15.0	0.35	10	5,5	no bubbles; not tacky

TABLE XIV-b

D SERIES--IRRADIATION

No.	PVA (gm)	SOLV. (ml)	CROSSLINKING AGENT	(ml)	Conc. (%)	COMPOSITION PVA (wt.%)	C.L. (wt.%)	DOSE Total (mrads)	Hist. (mrads)	OBSERVATIONS AFTER IRRADIATION
D-13	1.000	8.00	AMA	7.00	0.5	10.0	0.35	10	5,5	no bubbles; not tacky
D-14	0.500	8.00	AMA	7.00	0.5	5.0	0.35	10	5,5	no bubbles; not tacky
D-15	3.000	8.00	TEGDM	5.50	0.54	35.3	0.30	10	5,5	many bubbles; not tacky
D-16	3.000	8.00	TEGDM	7.00	0.54	30.0	0.38	10	5,5	many bubbles; not tacky
D-17	3.000	8.00	TEGDM	8.40	0.54	25.0	0.38	10	5,5	no bubbles; not tacky
D-18	2.000	8.00	TEGDM	7.00	0.54	20.0	0.38	10	5,5	no bubbles; not tacky
D-19	2.000	8.00	TEGDM	9.31	0.54	15.0	0.38	10	5,5	no bubbles; not tacky
D-20	1.000	8.00	TEGDM	7.00	0.54	10.0	0.38	10	5,5	no bubbles; not tacky
D-21	0.500	8.00	TEGDM	7.00	0.54	5.0	0.38	10	5,5	shrank from sides
D-22	3.000	8.00	---	----	----	35.3	0.00	10	5,5	many bubbles; not tacky
D-23	3.000	8.00	---	----	----	30.0	0.00	10	5,5	many bubbles; not tacky
D-24	3.000	8.00	---	----	----	25.0	0.00	10	5,5	bubbles;not tacky

TABLE XIV-c

D SERIES--IRRADIATION

NO.	PVA (gm)	SOLV. (ml)	CROSSLINKING AGENT	(ml)	Conc. (%)	COMPOSITION PVA (wt.%)	C.L. (wt.%)	DOSE Total (mrads)	Hist. (mrads)	OBSERVATIONS AFTER IRRADIATION
D-25	2.000	8.00	---	----	----	20.0	0.00	10	5,5	few bubbles; not tacky
D-26	2.000	8.00	---	----	----	15.0	0.00	10	5,5	no bubbles; not tacky
D-27	1.000	8.00	---	----	----	10.0	0.00	10	5,5	shrank from sides
D-28	0.500	8.00	---	----	----	5.0	0.00	10	5,5	shrank from sides

TABLE XV-a

D SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	W(OA) (gm)	W(OW) (gm)	W(SA) (gm)	W(SW) (gm)	OBSERVATIONS AFTER SWELLING	W(D) (gm)
D-01	MBA	35.3	1.75	8.2457	---	15.0376	.6486	no bubbles	3.1390
D-02	MBA	30.0	2.1	9.8590	---	16.1163	.7133	no bubbles	3.2736
D-03	MBA	25.0	2.1	11.7872	.5532	17.6226	.7512	no bubbles	3.2710
D-04	MBA	20.0	2.1	12.2924	.4399	12.3033	.5209	no bubbles	2.3377
D-05	MBA	15.0	2.1	10.4930	.1333	12.1718	.4707	no bubbles	2.1699
D-06	MBA	10.0	2.1	8.3534	.3050	6.8200	.3031	no bubbles	1.2261
D-07	MBA	5.0	2.1	3.9282	.1590	3.5127	.1573	opaque	0.6136
D-08	AMA	35.3	0.275	8.0246	---	27.2003	.2736	bubbles	3.0293
D-09	AMA	30.0	0.35	9.4270	---	24.1503	---	bubbles	2.9345
D-10	AMA	25.0	0.35	11.6110	.4570	---	---	dissolved	---
D-11	AMA	20.0	0.35	10.3657	---	16.5750	.3227	no bubbles	1.9592
D-12	AMA	15.0	0.35	12.6382	.4120	18.0652	.4531	no bubbles	1.9343

TABLE XV-b

D SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	W(OA) (gm)	W(OW) (gm)	W(SA) (gm)	W(SW) (gm)	OBSERVATIONS AFTER SWELLING	W(D) (gm)
D-13	AMA	10.0	0.35	8.1400	.2118	8.7777	.2206	no bubbles	.9402
D-14	AMA	0.5	0.35	6.4916	.1103	4.6100	.1073	no bubbles	.4606
D-15	TEGDM	35.3	0.3	8.2038	---	16.6469	.6315	no bubbles	2.9705
D-16	TEGDM	30.0	0.38	9.6568	---	17.8404	.5111	no bubbles	3.1273
D-17	TEGDM	25.0	0.38	11.5914	.6604	17.8674	.6744	no bubbles	2.9786
D-18	TEGDM	20.0	0.38	10.5657	.4726	12.6725	.4650	no bubbles	2.0706
D-19	TEGDM	15.0	0.38	12.4540	.4650	12.9558	.4596	no bubbles	2.0846
D-20	TEGDM	10.0	0.38	6.6990	.1960	5.4306	.1898	no bubbles	.8479
D-21	TEGDM	5.0	0.38	3.9040	.1113	3.4172	.1088	no bubbles;	.4682
D-22	---	35.3	0.0	8.2350	---	16.2434	---	bubbles	3.1062
D-23	---	30.0	0.0	9.6718	---	17.8602	---	bubbles	3.0143
D-24	---	25.0	0.0	11.5463	.2183	17.4331	.5320	no bubbles	2.9280

TABLE XV-c

D SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	W(OA) (gm)	W(OW) (gm)	W(SA) (gm)	W(SW) (gm)	OBSERVATIONS AFTER SWELLING	W(D) (gm)
D-25	---	20.0	0.0	9.7574	.3635	12.4736	.4501	no bubbles	1.9744
D-26	---	15.0	0.0	12.8102	.3900	12.1677	.4562	no bubbles	2.0021
D-27	---	10.0	0.0	7.8887	.2138	5.8965	.2301	no bubbles	.9652
D-28	---	5.0	0.0	2.4711	.0535	2.2351	.0767	no bubbles	.3356

TABLE XVI-a

D SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	V(P) (cc)	V(R) (cc)	V(S) (cc)	v(R)	v(S)	v(2m)	q
D-01	MBA	35.3	1.75	2.474	7.611	14.447	.325	.171	0.527	1.898
D-02	MBA	30.0	2.1	2.580	9.246	15.465	.279	.167	0.597	1.676
D-03	MBA	25.0	2.1	2.578	11.182	16.939	.230	.152	0.659	1.518
D-04	MBA	20.0	2.1	1.842	11.909	11.830	.155	.156	1.005	0.995
D-05	MBA	15.0	2.1	1.710	10.133	11.748	.169	.145	0.861	1.162
D-06	MBA	10.0	2.1	0.966	8.065	6.543	.120	.148	1.232	0.811
D-07	MBA	5.0	2.1	0.484	3.776	3.369	.128	.144	1.121	0.892
D-08	AMA	35.3	0.275	2.387	7.389	26.657	.323	.0895	0.277	3.607
D-09	AMA	30.0	0.35	2.312	8.794	23.595	.263	.0980	0.373	2.683
D-10	AMA	25.0	0.35	---	9.986	---	--	---	---	---
D-11	AMA	20.0	0.35	1.544	9.986	16.317	.155	.0946	0.612	1.634
D-12	AMA	15.0	0.35	1.524	12.251	17.683	.124	.0862	0.693	1.443

TABLE XVI-b

D SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	V(P) (cc)	V(R) (cc)	V(S) (cc)	v(R)	v(S)	v(2m)	q
D-13	AMA	10.0	0.35	0.741	7.944	8.591	.0933	.0862	0.925	1.081
D-14	AMA	5.0	0.35	0.363	6.394	4.521	.0568	.0803	1.414	0.707
D-15	TEGDM	35.3	0.3	2.341	7.569	16.080	.309	.146	0.471	2.124
D-16	TEGDM	30.0	0.38	2.464	9.025	17.399	.273	.142	0.519	1.928
D-17	TEGDM	25.0	0.38	2.347	10.953	17.262	.214	.136	0.634	1.576
D-18	TEGDM	20.0	0.38	1.632	10.113	12.256	.161	.133	0.825	1.212
D-19	TEGDM	15.0	0.38	1.642	12.013	12.546	.137	.131	0.957	1.044
D-20	TEGDM	10.0	0.38	0.668	6.516	5.262	.102	.127	1.238	0.808
D-21	TEGDM	5.0	0.38	0.369	3.800	3.322	.0971	.111	1.144	0.874
D-22	---	35.3	0.0	2.448	7.600	15.656	.322	.156	0.485	2.060
D-23	---	30.0	0.0	2.375	9.040	17.279	.263	.137	0.523	1.911
D-24	---	25.0	0.0	2.307	10.918	16.969	.211	.136	0.643	1.554

TABLE XVI-c

D SERIES--IRRADIATION

NO.	C.L.	COMPOSITION PVA (wt.%)	COMPOSITION C.L. (wt.%)	V(P) (cc)	V(R) (cc)	V(S) (cc)	v(R)	v(S)	v(2m)	q
D-25	---	20.0	0.0	1.556	9.413	12.072	.165	.129	0.780	1.282
D-26	---	15.0	0.0	1.578	12.445	11.758	.127	.134	1.058	0.945
D-27	---	10.0	0.0	0.760	7.690	5.689	.0989	.134	1.352	0.740
D-28	---	5.0	0.0	0.264	2.427	2.167	.109	.122	1.118	0.894

VIII. APPENDIX

A. Serial Dilution Technique for Crosslinking Monomers in Series A--Irradiation

The maximum weight of crosslinking agent added to a PVA sample was the solubility of the monomer times 8 ml--the amount of solvent added to the 2.00 gm PVA samples to obtain a 20% PVA solution. The other two concentrations were selected arbitrarily at approximately two and five-fold dilutions of this maximum concentration. The cross-linking monomer wt. % of the total 10. gm sample was easily calculated as the (weight of monomer)/10 gm, assuming the density of 20% PVA was unity. An example follows.

The weights of allyl acrylate--AA--and the corresponding total wt. % AA of the three involved samples were 0.08 gm, 0.04 gm, and 0.01 gm and 0.8 wt.%, 0.4 wt.%, and 0.1 wt.% or a total of .13 gm--.138 ml (see Table IV).

1. Dilution to maximum solubility

Letting X be the grams of water added, the equation for the final wt. % C.L. agent in the solvent was

$$\frac{0.13 \text{ gm}}{.13 \text{ gm} + X \text{ gm } H_2O} = \frac{0.08 \text{ gm C.L.}}{8.0 \text{ ml of solution}}$$

$$X = 12.87 \text{ gm water added}$$

The total wt.% of monomer in sample A-1 after receiving 8 ml--0.08 gm of monomer--of this solution was

$$\frac{0.08 \text{ gm C.L. agent}}{10 \text{ gm total}} = 0.8\%$$

and leaving a solution of

$$\frac{0.05 \text{ gm C.L. agent}}{5.0 \text{ gm solution}}$$

2. Second dilution

Following the procedure for the first dilution

$$\frac{0.05 \text{ gm C.L. agent}}{5.0 \text{ gm soln.} + X \text{ gm } H_2O} = \frac{0.04 \text{ C.L. agent}}{8.0 \text{ ml soln.}}$$

$$X = 5 \text{ gm } H_2O \text{ added}$$

The total wt.% of monomer in sample A-2 after receiving 8 ml--0.04 gm of AA--of this solution was

$$\frac{0.04 \text{ gm C.L. agent}}{10 \text{ gm total}} == .4\%$$

and leaving a solution of

$$\frac{0.01 \text{ gm C.L. agent}}{2.0 \text{ gm soln.}}$$

3. Third dilution

Adding 6.0 ml of water to the remaining solution gave

$$\frac{0.01 \text{ gm C.L. agent}}{8.0 \text{ gm total}}$$

The total wt.% of monomer in sample A-3 after receiving all 8.0ml of this solution was

$$\frac{0.01 \text{ gm C.L. agent}}{10 \text{ gm total}} = 0.1\%$$

B. Total Wt.% of Each Crosslinking Monomer in Series B--Irradiation

MONOMER

Name	Vol. (conc.)	H_2O	PVA	Wt.% Monomer
AA	4 ml (1%)	4 ml	2 gm	$\frac{4(.01)}{4+4+2} = 0.4\%$
AMA	4 ml (.5%)	4 ml	2 gm	$\frac{4(.005)}{4+4+2} = 0.2\%$
MBA	4 ml (3.0%)	4 ml	2 gm	$\frac{4(.03)}{4+4+2} = 1.2\%$
DAA	4 ml (4.0%)	4 ml	2 gm	$\frac{4(.04)}{4+4+s} = 1.6\%$
TEGDM	4 ml (0.54%)	4 ml	2 gm	$\frac{4(.54)}{4+4+2} = 0.22$

For these dilute solutions all densities can be assumed unity.

C. Crosslinking Monomer Wt. % Calculations for Series D--Irradiation

As indicated on page 59, the quantity of monomer added to samples of decreasing PVA concentration must also decrease to maintain a constant total weight per cent of monomer. If for example, the added monomer was not diluted as the PVA concentration decreased, the following would be the effect on the total wt. % of monomer for .5% by weight AMA:

PVA wt.%	PVA(gm)	Solvent(gm) (.5% AMA)	Total monomer wt.%
30	3	7	.35
25	3	9	.375
20	2	8	.4
15	2	11.3	.426
10	1	9	.455
5	.5	9.5	.475

To avoid the unnecessary complications which might arise from not maintaining a constant monomer wt.%, the following method was utilized.

The total monomer wt.%, which is to remain constant, is givin in eq. C-1.

(C-1)

$$\text{total monomer wt.\%} = \frac{\left(\begin{matrix}\text{weight of}\\ \text{added solvent}\end{matrix}\right) \times \left(\begin{matrix}\text{monomer wt.\% of}\\ \text{added solvent}\end{matrix}\right)}{\left(\begin{matrix}\text{dry weight}\\ \text{of PVA}\end{matrix}\right) + \left(\begin{matrix}\text{weight of}\\ \text{added solvent}\end{matrix}\right)}$$

rearranging equation C-1 yields C-2.

$$\text{monomer wt.\% of added solvent} = \frac{\text{total monomer wt.\%}}{\left(\frac{\text{weight of added solvent}}{\text{total weight of sample}}\right)} \qquad \text{(C-2)}$$

$$= \frac{\text{total monomer wt.\%}}{\text{\% solvent}}$$

Finally,

$$\text{monomer wt.\% of added solvent} = \frac{\left(\text{vol. of added monomer}\right)\left(\begin{matrix}\text{original}\\ \text{monomer}\\ \text{wt.\%}\end{matrix}\right)}{\text{total solvent vol.}} \qquad \text{(C-3)}$$

For a 25% PVA solution, a .5% AMA gave a total monomer wt.% of .375% and not the desired .35%. From (C-2)

$$\text{monomer wt.\% of added solvent} = \frac{.0035}{.75}$$

Using (C-3)

$$\text{vol. of added monomer} = \frac{\text{total solv. vol.} \ \frac{.0035}{.75}}{.005} = 8.4$$

Thus instead of adding 9.0 ml of .5% AMA, 8.4 ml of .5% AMA +.6ml of water are added.

In calculating the total monomer wt.% in Series D, the value at 30% PVA was selected as the maximum. 35% PVA was later run and treated as if it were 30% PVA, as the maximum soluble concentration of the crosslinking monomers had already been added to the 30% samples. Thus, the

total crosslinking agent concentrations for the 35% PVA samples were slightly less than the given values in Table XIV.

D. NOMENCLATURE

AA--------Allyl acrylate

AMA-------Allyl methacrylate

C_M ------Chain transfer constant for monomer

C.L.------Crosslinking

DAA-------Diallylamine

$k(_{tr,i})$---constant of chain transfer with initiator

$k(_{tr,m})$---constant of chain transfer with monomer

$k(_{tr,s})$---constant of chain transfer with solvent

MBA-------N'-N'-methylene-bis-acrylamide

q---------swelling ratio by volume; V(S)/V(R)

TEGDM-----Tetra-ethylene-glycol-dimethacrylate

v(2m)-----Volume fraction of the polymer at swelling equilibrium; 1/q

v(P)------Volume of the dryed polymer network

V(R)------Volume of a relaxed polymer network

v(R)------Volume fraction of polymer in the relaxed state

V(S)------Volume of a swollen polymer network

v(S)------Volume fraction of polymer in the swollen state

W(D)------Weight of the dryed polymer

W(OA)-----Weight of the polymer gel in air prior to swelling

W(OW)-----Weight of the polymer gel in water prior to swelling

W(SA)-----Weight of the polymer gel in air at swelling equilibrium

W(SW)-----Weight of the polymer gel in water at swelling equilibrium

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